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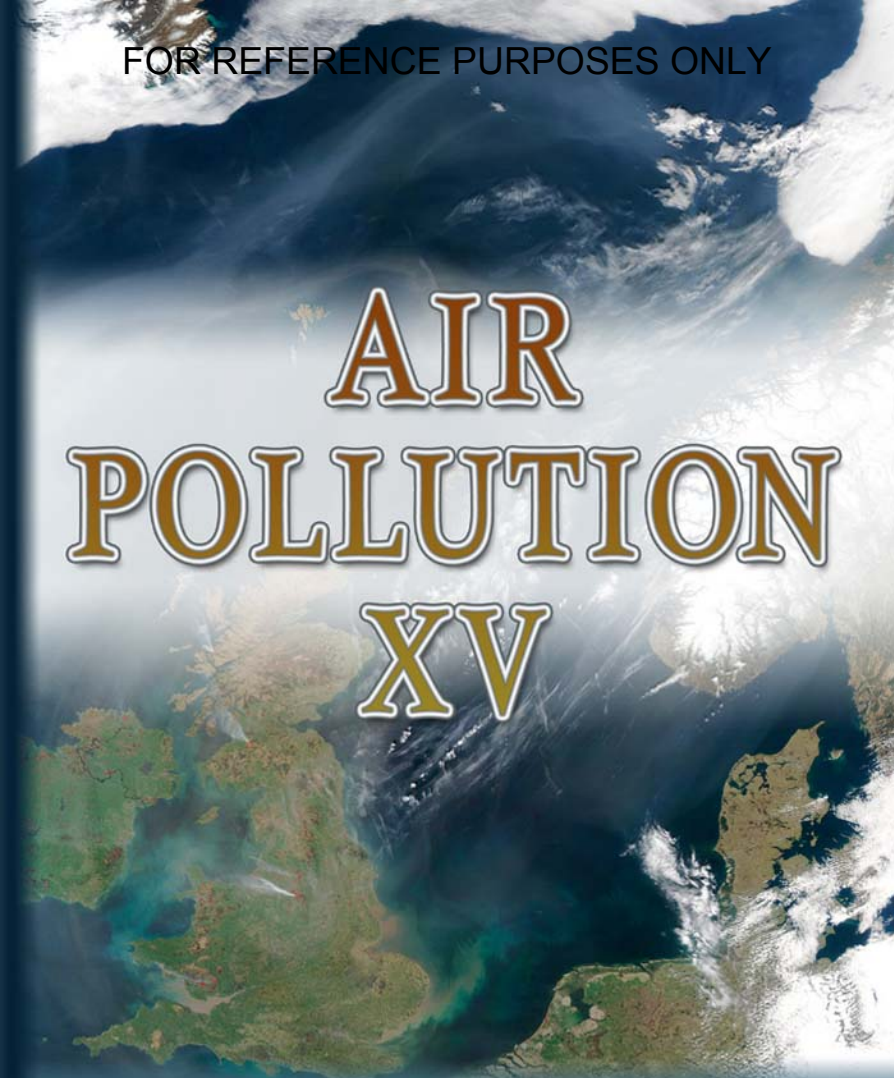

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Preface

This volume contains most of the contributions presented at the Fifteenth International Conference on Modelling, Monitoring, and Management of Air Pollution. This International Scientific Meeting began its course in Monterrey, Mexico in 1993 and has been successfully reconvened since.

Air pollution nowadays represents one of the most challenging issues that humankind is facing. On the one hand, with the growth of the economies of emerging countries leading to an increase in the demand for more energy, the prevention of air deterioration by means of controlling atmospheric emission has become an urgent task. On the other hand, the mitigation strategies for traditional, but persistent air pollution problems, such as particulate and photochemical pollution, soil eutrophization and acidification remain important issues.

Science has, in this process, a crucial role to play in the prediction, understanding and mitigation of atmospheric pollution phenomena. Furthermore, the development of analysis tools is making it possible to accomplish air quality assessment using modelling techniques that can be applied on a global scale, providing technical support to policy-makers. Air quality networks continue to be enhanced, offering monitoring and forecasting operations in real time

The need for awareness of the population in the process of implementing policies is fundamental towards the success of legislative efforts. The accessibility of the population to education and scientific knowledge is important to help promote a better understanding of the policies adopted.

This book includes the latest developments in air pollution modeling, air quality management, urban air management, transport emissions, emission inventory, comparison of model and experimental results, monitoring and laboratory studies, global and regional studies, aerosols and particles, climate change and air pollution, atmospheric chemistry, indoor pollution, environmental health effects and remote sensing.

The Editors would like to thank the contribution of the Authors, and acknowledge the assistance of the members of the International Scientific Advisory Committee who helped to organise the conference and to review the submitted papers.

The Editors
Algarve, Portugal, 2007

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Introduction

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Fifty years air pollution research and policy in the EU

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Abstract

Despite the fact that air pollution has been observed since Roman times, and thatin past centuries some limited, rather local actions have already been taken, it required several air pollution episodes with serious health impacts before air pollution management really started in a limited number of cities, regions or countries. A noteworthy example is the famous London smog episode in 1952 that triggered a systematic approach locally and in some other European countries. Based on an "air pollution system" approach, some major evolutions and achievements in the EU are highlighted in this paper for the following subsystems: emissions, immissions, air quality guidelines/standards and modelling.
Keywords: air pollution, historical review, research, policy, monitoring, modelling, management.

1 Introduction

Air pollution, especially in cities, is not at all a new problem. Already in the writings of the Roman philosopher Seneca air pollution appears. Many centuries later, namely in 1661, J. Evelyn [1] mentioned in his "Fumifugium" the influence of industrial emissions on human health, plants and animals, as well as the transboundary exchange of pollutants between England and France. He even suggested remedial actions such as higher chimneys and industrial zones outside the city. Some 200 years later R.A. Smith published a detailed report on the chemical composition of rainwater as a function of the distance to the centre of the city of Manchester. He was also the inventor of the expression "acid rain" in his book [2]. Around the same time the first steps in cleaning flue gases were set too. A more complete review of this is given in "A history of flue gas

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desulphurization systems since 1850", JAPCA, Vol. 27, No.10, 1977. Note, as one illustrative example, that the UK's 1875 Public Health Act contained already a smoke abatement section to try to reduce smoke pollution in urban areas.

Despite this growing awareness and knowledge as a function of time, and due to the continuously increasing urbanization and industrialization, serious, less or more well documented catastrophic air pollution episodes with major health impacts started in 1930 with the smog episode in the Meuse valley in Belgium, followed by "Donora, Pennsylvania 1948", "Poza Rica, Mexico 1950", "London, UK 1952", "New York, US 1953", … Those accidents triggered large scale ambient air pollution measurements in different cities, regions and countries. Daily measurements of smoke and sulphur dioxide were started in the City of London in 1954 as well as the determination of sulphuric acid, NO_x, CO and CO_2 during periods of high pollution [3]. In the US the National Air Sampling Network became operational in 1953, and hourly readings of NO_x, hydrocarbons, CO, SO_2, O_3 and particulates were started in 1955 by the Los Angeles Air Pollution Control District. Many European cities and regions followed in the early sixties [4]. Large scale air pollution monitoring, modelling, and management obviously started some 40 to 50 years ago.

2 The air pollution system

Before entering into the description of some of the major changes and/or improvements realized over the past decades, it is worthwhile to have a look at the overall air pollution system from the engineering point of view. As shown in figure 1 air pollution problems, and environmental problems in general, are inherent to whatever human activity. Making products, running processes or rendering services always requires an input of energy and mass into a given (sub)system to get a useful output from the same (sub)system. But, between input and output fractions of the input energy and mass are always lost and escape into the environment. That, the use of those products and the final removal at the end of their life as products and processing/servicing equipment, are the origin of whatever manmade pollution.

More specific for the air pollution system, all problems start with the emission of gaseous or solid pollutants from point, line and surface sources. Once in the atmosphere they are transported, dispersed and eventually transformed in the "transmission" subsystem leading finally to ground level concentrations or immissions and wet or dry deposition on surfaces or in water. Via direct pathways – be it during transmission (cloud shine, electromagnetic radiation, noise) or from immission/deposition (ground shine, ingestion, inhalation, skin deposition) – and via indirect pathways (mainly the food chain) people, the ecosystem and all non-living matter risks to be exposed during shorter or longer periods of time. In order to avoid unwanted effects those levels of exposure have to be limited in time and space and for that purpose Air Quality Guidelines (AQG) have to be defined by international organizations such as the World Health Organization (WHO). In an ideal world those levels, below which the risk for effects is rather improbable, should be enforced in all countries, but

the reality is different. Indeed "socio-economic constraints", being a function of the specific country or even region and (urban) area, make it impossible to switch in one step and immediately from the present polluted situation to the ideal one. Therefore Air Quality Standards (AQS), taking into account the local physical, financial, economic and political constraints, do generally enforce higher air pollution levels (limit or alert values) than the ones in the international air quality guidelines (reference, guide or target values). Lowering ambient levels does of course not happen by only introducing AQSs or AQGs. The only way to realize that is to reduce or eliminate emissions by an emission abatement policy (legal emission limits) and appropriate technologies and means, be it end-of-pipe or (preferentially) in-process or at the input. Fortunately more and more regulation and legislation (eco-norms) enter into force at the level of the products and processes we make and use in order to avoid or reduce air pollution from cradle to grave.

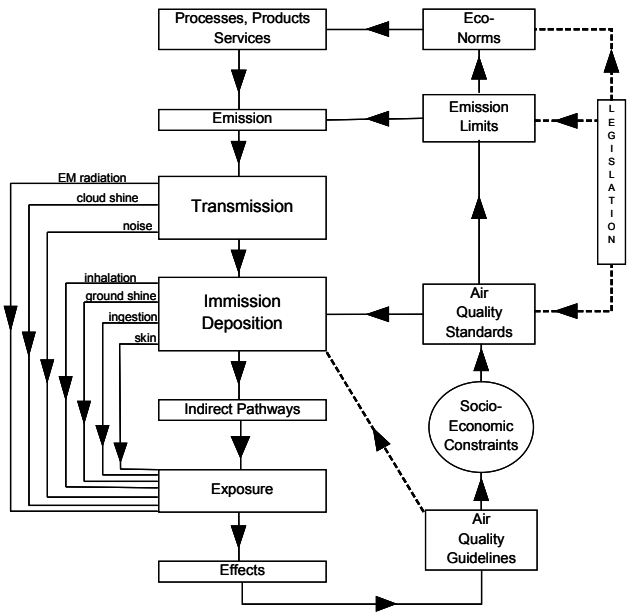

Figure 1: The air pollution system.

Over the past 40 to 50 years major improvements have been realized in each of the subsystems of the overall air pollution system sketched in figure 1. In what follows the following topics will be highlighted in somewhat more detail with the focus on the European Union Member States: emissions regulated and reduced, ambient air pollutants levels decreased, more stringent AQGs and AQSs, modelling: from nomogram to PC or workstation.

3 Emissions regulated and reduced

As already mentioned in the introduction one of the first actions to curb ambient air pollution levels was to increase chimney heights. In the aftermath of the Great London Smog in 1952 the UK government passed the Clean Air Act 1956 to control industrial sources by the use of tall chimneys. Many other countries took similar actions by imposing formulas or nomograms to calculate the required chimney heights such as the well-known German VDI-2289 Richtlinien in 1963 [5,6].

But pretty soon people realized that this was not the best solution as whatever mass released in the air must come down somewhere, some day to the earth's surface. Already in the sixties scientists demonstrated the interrelationship between sulphur emissions in continental Europe and the acidification of Scandinavian lakes. The 1972 UN Conference on the Human Environment in Stockholm signaled the start for active international cooperation to combat acidification. This leads in 1979 to the Geneva Convention on Long-range Transboundary Air Pollution, and after much intermediate legislation to the EU-directive 2001/81/EC or NEC-directive [7]. Table 1 summarizes the presently obtained and targeted reductions in acidifying emissions for the EU-15 and two specific countries

Table 1: Emission trends and NEC*-ceilings 2010 (kt/y).

		1980	1990	2000	2010*
SO_2	Belgium	828	356	172	99
	Germany	7514	5326	636	520
	EU-15	26698	16500	6077	3850
NO_x	Belgium	442	358	329	176
	Germany	3334	2846	1634	1051
	EU-15	13100	13410	9931	6519
NH_3	Belgium	89	107	86	74
	Germany	835	736	607	550
	EU-15	3617	3634	3343	3110

Setting global, country specific emission limits for certain pollutants is of course not sufficient to curb the emissions. Emissions have to be specifically regulated for a wide variety of processes and installations and their relevant pollutants. One of the first European countries to do so was Germany with its "Technische Anleitung zur Reinhaltung der Luft" or TA Luft in 1964 with formalized licensing procedures (emission standards, minimum stack height, ambient monitoring) for environmentally relevant plants. Many other countries followed that example by similar regulations. Twenty years later directive 84/360/EEC had to start eliminating unequal competition between industries in the Member States due to too large differences between all those national laws. Later on this was refined and extended by the Large Combustion Plants directive (88/609/EEC) and the IPPC directive (96/61/EEC). With respect to industrial

risk mention must be made of the Seveso directive (96/82/EC), which by the way was approved 20 years after the Seveso disaster on July 10, 1976.

Emissions of mobile sources were somewhat overlooked in the beginning but, following similar regulations in Germany in 1968 and in France 1969, the European Communities issued CO and hydrocarbon limits for new petrol cars by directive 70/220/EEC and for diesels by directive 72/306/EEC. In the same period Pb in leaded gasoline was reduced in many countries, or by voluntary actions of the refineries or by legislation. Directive 78/611/EEC harmonized those national initiatives at the EU-level and set the target value at 0,15 Pb/liter gasoline. Three years earlier something similar had already been done for the sulphur content in liquid fuels by directive 75/716/EEC. Over the years all those limitations became more stringent and led e.g. for lead to directive 85/210/EEC requiring the introduction of unleaded gasoline, not containing more than 5% benzene (by volume) as of October 1989. The introduction of low emission vehicles, e.g. using 3-way catalytic convertors, was already in 1980 encouraged by tax incentives in West Germany. By directive 88/76/EEC new gasoline vehicles had to be designed to operate with 95 RON unleaded gasoline.

4 Ambient air pollution levels decreased

When starting their daily SO_2 and smoke measurements in London in 1954, Commins and Waller measured yearly averages of respectively 377 and 160 µg/m³ [3]. In the early sixties those levels were still high with values between 438 and 253 for SO_2 and 100 to 60 µg/m³ for smoke. Daily SO2 extremes were systematically above 1000 µg/m³ on a yearly basis, with peak values exceeding 3000 µg/m³ as daily averages, and even above 5000 µg/m³ on an hourly basis. In other European cities the situation was not much better with the following yearly averages (µg/m³) for SO_2: 250 in Hamburg, 200 in Paris, 170 for the Ruhr area in Germany, etc… Half-hourly values in Bochum, Germany sometimes exceeded 1 mg/m³ in 1961 [8]. Although the situations ameliorated gradually as a function of time, the early seventies still showed yearly averages clearly above 100 µg SO_2/m³ and between 50 and 100 µg smoke/m³ in many European urban areas. Very polluted cities were obviously Madrid and Milan [4].

Over the past 40 years ambient SO_2 – and smoke – or particulate levels have been drastically reduced and are nowadays in general below the WHO air quality guidelines. This has been realized by much lower sulphur content of liquid fuels, the increased use of sulphur free natural gas, the drastic reduction of coal use, by chances in the industrial processes and by flue gas desulphurization.

The situation for ambient particulate pollution is not all that clear. As long as (black) smoke [9] was measured as indicator for this pollution, a systematically decreasing trend was observed. Taking Antwerpen in Belgium as example 60 µg smoke/m³ was measured as yearly average by the end of the sixties against some 20 µg/m³ by the end of the 80s and 12 µg/m³ in 1995. But if we switch to PM10, the important particulate pollution indicator since more than 10 years, the same city reports 35 µg/m³ for the yearly average in 2005 with more than

40 exceedances of the daily limit value of 50 μg/m³ in the AQS of the EU. This is not exceptional in the EU Member States as is clearly described in [10].

The same reference [10] also shows that after many years of continued efforts, and despite global, but sometimes slow downward trends, the NO_2 situation is not completely satisfactory, especially not in busy streets in large urban areas. Indeed at many monitoring stations a number of violations of the 200 μg NO_2/m³ AQS for half hourly values is still observed today. Even yearly averages did sometimes hardly decrease with for example Paris where the 80 to 90 μg NO_2/m³ observed in the nineties is still present today. It seems even more difficult to get ambient ozone levels down. Since more than 20 years almost every very good summer period, with stable meteorological conditions, creates O_3 problems downwind many urban agglomerations or large industrialized regions. In an European Environment Agency report [11] we read: "In the summer 2005 levels of ground-level ozone were high in southern Europe with widespread exceedances of the information threshold value (180 μg/m³) laid down in the ozone directive (2002/3/EC). The frequency of exceedances of the information threshold was similar to earlier years, except for the summer of 2003, which had a record number of exceedances. The highest one-hour ozone concentration in summer 2005 (361 μg/m³) was observed in Portugal. Other high hourly ozone concentrations between 260 and 300 μg/m³ were reported from Greece, Italy, France, Romania and Spain. The directive's long-term objective to protect human health, an ozone concentration of 120 μg/m³ over 8 hours, was extensively exceeded in the EU and other European countries. In large parts of Europe the target value to protect human health was also exceeded."

Some other harmful pollutants seem nevertheless largely under control after many years of action. Lead in urban streets is for instance one example. Indeed yearly average levels measured today in busy streets of urban agglomerations are in the range 20 ng/m³ while 30 years ago 4 μg Pb/m³ was not a really surprising value. Even around lead smelters the situation improved drastically, although exceedances of the 0,5 μg Pb/m³ yearly average AQS are still possible at a very limited number of monitoring sites. Other examples of ambient air pollutants that significantly decreased over the past decades are: CO in busy streets, dioxins in the vicinity of specific industrial plants or waste incinerations, benzene and benzo-a-pyrene in cities,… to cite only a few representative examples.

5 More stringent AQGs and AQSs

As early as 1959 the World Health Organization (WHO) convened a group of experts to evaluate the possible influence of air pollution on lung cancer. Quite some years later the WHO published in 1972 its first guidelines for SO_2 and particulates/smoke in air. Several Env. Health Criteria reports for specific pollutants followed as a function of time, and the original AQGs were regularly updated and extended. A good review of the state of expert knowledge and corresponding AQGs is given in [12]. In the most recent 2005 global update [13] the following AQGs for some priority pollutants are:

Table 2: Updated WHO a quality guideline values [13].

Pollutant	Averaging time	AQG value
Particulate matter		
$PM_{2.5}$	1 year	10 μg/m³
	24 hour (99th percentile)	25 μg/m³
PM_{10}	1 year	20 μg/m³
	24 hour (99th percentile)	50 μg/m³
Ozone, O_3	8 hour, daily maximum	100 μg/m³
Nitrogen dioxide, NO_2	1 year	40 μg/m³
	1 hour	200 μg/m³
Sulfur dioxide, SO_2	24 hour	20 μg/m³
	10 minute	500 μg/m³

One of the first, if not the first set of regional AQSs had already appeared in 1960 in Nordrhein-Westfalen, Germany. The first, legally binding country specific air quality standards were possibly enacted in Japan in 1968. The US followed with its Clean Air Act of 1970, as well as many other countries. In Europe it lasted nevertheless quite some time before certain countries started action. The directive 80/779/EEC of 15 July 1980 on air quality limit values and guide values for sulphur dioxide and suspended particulates was not only the first AQS directive in the EU, but it also forced some of its Member States to finally start action and, for all 9 countries, to bring their national legislation in line with the limit and guide values specified in that directive. Note also that the limit values in 80/779/EEC were significantly higher than the WHO air quality guidelines of those days. As one example: AQG for yearly average and maximum daily concentration for SO_2 were respectively 40 to 60, and 100 to 150 μg/m³ versus AQS limit values of 140 and 250 to 350 μg/m³ (as 98-percentile) in the directive.

As can be seen in Table 2 the WHO air quality guidelines obviously became more stringent (= lower ambient levels) for SO_2 as a function of time, and this also holds for all other pollutants. AQS have followed that evolution in the successive adaptations of EU and national legislations. In 1996 the European Council published its framework directive 96/62/EC with as aim to define the basic principles of a common strategy to:

- define and establish, by means of daughter directives, objectives for ambient air quality in the Community designed to avoid, prevent or reduce harmful effects on human health and the environment as a whole;
- assess the ambient air quality in Member States on the basis of common methods and criteria;
- obtain adequate information on ambient air quality and ensure that it is made available to the public, inter alia by means of alert thresholds;
- maintain ambient air quality where it is good and improve it in other cases.

Up to now the following daughter directives, bringing the legal limits of ambient air levels almost completely in line with the present day WHO AQGs [12, 13], and also defining some alarm levels, were published:

- 99/30/EC for SO_2, NO_2, PM_{10} and Pb;
- 00/69/EC for CO and benzene;
- 02/03/EC for O_3, and 04/107/EC for As, Cd, Ni, Hg and PAHs.

It can be expected that levels and exposure durations in those directives do change in the future – normally downward for the levels – and that still other ambient pollutants will be regulated.

The driving forces for those monotonically decreasing so-called safe ambient levels are multiple. Possibly the main ones are: better knowledge of the overall air pollution system, increased and more generalized public awareness, improved insight in the health and other effects of air pollution, the ever increasing measuring and monitoring capabilities, the ICT and industrial technology progress and improvements in general.

6 Modelling: from nomogram to PC and workstation

The main problem to completely evaluate ambient air pollution in a given area, region or country is the fact that air pollution levels are a function of time and space. Although major developments and progress have already been made for airborne or spaceborne monitoring, trying to simultaneously measure pollutants at ground level as a function of time and space over larger areas, it must be admitted that the obtained information is still largely insufficient. A second problem in ambient air pollution measurements are the costs of intensive and prolonged monitoring. Finally it is not possible by means of measurements to forecast the air pollution evolution as a function of changing meteorological conditions, emissions, legislation, town and country planning, industrial and human activities, … If we could mathematically simulate the blocks "emission, transmission and immission/deposition" in the air pollution system (Figure 1), what preceeds would become possible in a fast and cheaper way. Atmospheric transport and dispersion modelling is trying to do that since many decades.

Already since the 30s concentrations were estimated by means of the equations and dispersion parameters of e.g. O. Sutton and C. Bosanquet. In 1957 Hay and Pasquill presented experimental evidence that the vertical distribution of elevated point releases of particles was related to the standard deviation of the wind elevation angle at the point of release. In the same year H. Cramer derived a diffusion equation incorporating standard deviations of the Gaussian distributions. Values for diffusion parameters based on field tests followed, as well as a method to derive the spread of pollutants from wind fluctuation records. F. Pasquill proposed in 1961 a method for estimating diffusion, when such detailed data were not available, as well as the "stability class" concept. Gifford converted in the same year Pasquill's values of angular spread and height into sigma $_Y$ and sigma z formulas. In 1970 D. Bruce Turner published his well-known "Workbook of atmospheric dispersion estimates" [14], an excellent manual for, and summary of the atmospheric transport and dispersion knowledge

at that time, as well the start of the widespread use of bi-Gaussian modelling. Based on the compilation of formulas, graphs and chimney formulas, and the practical examples in Turner's workbook, the scientific community started almost immediately with the transfer of that knowledge to mainframe computers in one way or another. The modelling community was born, and the first NATO/CCMS International Technical Meetings on Air Pollution Modelling and its Application were organized in 1971 under the form of expert panels. In the following years those meetings evolved from panels to workshops to authoritative modelling conferences, with in 2007 the 29th edition.

The Gaussian plume model was the central air pollution model during the sixties and seventies, but in the 70s the solution of the full diffusion equation got more and more interest from the researchers. The various numerical methods to solve that set of differential equations formed an essential element in the next decades. The first photochemical models appeared in the same period too. Long-range air pollution modelling became an important topic in the early 80s, and the CEC e.g. started an indirect action research programme on the Safety of Thermal Water Reactors with long-range modelling as a specific topic. After 1985 the output of numerical meteorological models was more and more used as model input (the prognostic approach) i.o. meteorological observations (the diagnostic approach). In the last two decades no real inventions have been made except that models became more complex, tackled a wider variety of problems from very local (street canyons e.g.) to very complex (complicated topography, nested models etc…). All of this was only possible thanks to continuously increasing computer power and capabilities, a better and more detailed knowledge of the atmospheric characteristics, improved emission inventories, etc. For a more detailed historical survey of air pollution models reference is made to some relevant papers in [15]. Today, a wide variety of operational models exists as illustrated by the 113 models on the website of the European Topic Centre on Air and Climate Change (www.eea.europa.eu). Despite all what preceeds it is also true that the Gaussian transport and dispersion approach still forms, in one way or another, the basis of many, country specific regulatory models.

7 Conclusions

Major reductions in air pollutant emissions in the EU member states were realized during the past 50 years, resulting in drastic decreases of the ambient levels of many air pollutants. Despite this general improvement certain priority pollutants such as nitrogen oxides are not completely under control, while ambient ozone levels and small particulates are still, and sometimes systematically too high downwind major urban areas or industrial zones. The knowledge of the health impacts of air pollution significantly improved, resulting into lower and better underpinned air quality guidelines. The same holds for EU and national air quality standards and the many emission reduction and abatement regulations. Air pollution monitoring tools and networks became more accurate, sensitive and reliable, and cover today a wide range of specific pollutants or groups of pollutants. Modelling, originally almost manual tools of a

few experts became operational computer based tools for air pollution evaluation, forecasting and management for whatever air pollution problem. Air pollution monitoring and modelling go hand in hand today as reliable tools. Many problems nevertheless still exist and new ones will certainly appear. All of the above does therefore not mean that further developments and their practical implementation will stop today.

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Section 1
Air pollution in Portugal

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Air pollution and child respiratory diseases: the Viseu case study, Portugal

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Abstract

An urban area of inland Portugal, without severe air pollution problems as yet, was selected for this work, based on the fact that future development could lead to air quality degradation. To evaluate the influence of air pollution on 6 to 10 years old asthmatic children, environment and medical parameters were monitored. Children were selected based on the school health questionnaire validated and widely applied by the ISAAC project (International Study of Asthma and Allergies in Childhood) and submitted to medical tests at the hospital. At the same time, several field campaigns were realised to characterize the outdoor and indoor air quality of the study area in different seasons (winter and summer time). Measured parameters included meteorological data and ambient air concentrations of ozone (O_3), nitrogen oxide (NO), nitrogen dioxide (NO_2), carbon monoxide (CO), sulphur dioxide (SO_2), benzene, toluene, ethylbenzene and xylene (BTEX), measured continuously (3 mobile labs) and using diffusive tubes (indoor and outdoor), and also particulate matter (PM_{10} and $PM_{2.5}$), using high volume and low volume samplers. Preliminary results have shown that, although the study area has no air pollution problems as yet, high levels of some pollutants, like particulate matter, could be registered, especially at night. To understand the influence of dispersion conditions on air quality, mesoscale and local scale models were applied and validated with field campaign data.
Keywords: air pollution, respiratory diseases, exposure.

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1 Introduction

According to the European Environment Agency [1], indoor and outdoor air pollution are the environmental factors with the greatest impact on health in Europe and are responsible for the largest burden of environment-related disease. The estimates suggest that 20 million Europeans suffer from respiratory problems every day. The evaluation made under the CAFE programme found that in the EU about 350 000 people died prematurely in 2000, in particular from cardiovascular and cardiopulmonary disease, due to the outdoor air pollution caused by fine particulate matter ($PM_{2.5}$). This corresponds to an average loss of life expectancy of about 9 months for every EU citizen. According to WHO evaluation [2] air pollution was responsible for 100 000 deaths and 725 000 years of lost life each year in a selection of European cities within the WHO European region.

Asthma, a respiratory disease with societal costs estimated at EUR 3 billion/year, is increasing all over Europe [1]. Asthmatic persons, and particularly asthmatic children, are sensitive to air quality and several studies show a strong association between exposure to air pollution and the aggravation of asthma [3]. Childhood respiratory health/asthma is one of the four priority groups of diseases identified by the child-focused EU SCALE process and stated by the European Environment Agency as a priority on the European environment and health action plan [4].

2 The SaudAr project

SaudAr is the Portuguese acronym of the project "The Health and the Air we breathe", whose main objective is to contribute towards urban sustainable development by preventing air pollution problems and health related diseases in the future due to expected economical development.

This study has an interdisciplinary approach including researches from environmental and medical sciences, working together with local authorities, including the town municipality, local hospital, selected schools, industrial and trading association and an environmental research team from the local polytechnic institute.

The study encompasses four tasks: (i) case-study selection; (ii) current situation characterization, including economical, social, environmental and health aspects; (iii) future development scenarios impact assessment on air pollution and child health; (iv) development of an education and information programme. A more detailed project description is following presented.

2.1 Task 1 – Case-study selection

Ten Portuguese towns, located in the inland part of the country were chosen assuming that currently they do not present air pollution related problems. The town of Viseu was selected due to its strategic location, in the central Portuguese mainland region and near important road transport networks, and its projected high development in near future. This town has, simultaneously, the

highest population density (190 inhabitants.km^{-2}), the highest birth rate and the lowest mortality rate, in the group of the ten considered towns.

2.2 Task 2 - Current situation characterization

This task includes, besides census and statistical data, the evaluation of outdoor and indoor air quality and child health examination, performed in the course of the dedicated field campaigns.

The ISAAC (International Study of Asthma and Allergies in Childhood) questionnaire was applied to 805 children from 4 selected schools (2 located in town centre – *Massorim* and *Marzovelos* – and 2 in city suburbs – *Ranhados* and *Jugueiros*) to identify those presenting respiratory disease (sibilance). During the field campaigns these children attended the local hospital where the medical research team carried out several medical tests including respiratory function and allergy. At the same time the children's houses received an environmental technician that characterised the microbiological infestation (fungus and acarus) of microenvironments. Moreover, the air quality evaluation in the field campaigns involved also radon measurements at schools and children's houses, traffic counts in the most important roads and surface meteorological measurements. Besides the ground based information, radiosondes and tether-balloon soundings have been done.

This characterization is complemented with modelling results that provide a spatial overview of air quality levels at mesoscale and local scale, as well as urban hot-spots.

(a) (b) (c)

Figure 1: Child health evaluation at the local hospital (a), outdoor air pollutant measurement using passive samplers (b) and mobile air quality laboratory with high-volume PM samplers (c), during field campaigns.

2.3 Task 3 – Future scenarios impact assessment

Future scenarios are designed based on expected social and economic development. The municipality strategic development plan establishes the placement of different activities, changes in land use and defines the foreseen

structural dynamics, such as road transport networks, housing or industrial parks, being an important document to be taken into account.

To build future scenarios, specific indicators are used to calculate future air pollutant emissions inventories, considering the different emission sources (industry, residential, services, traffic and other). The numerical tools will be applied to estimate air quality changes related with future scenarios; afterwards the impact on child health will be assessed with the previously established indicators.

The scenarios analysis should provide information to help the municipality to prevent pollution problems in the future and redefine the strategic plan.

2.4 Task 4 - Development of an education and information programme

Major attention is given to public information and education with two main objectives: (i) changing people's habits and behaviour; (ii) get people involved and participating in the decision making process. Some already carried out and foreseen activities include: the development of partnership and meetings with local authorities and interest groups, children sensitization during field campaigns, seminars, development of an internet site with a specific page for children, using simple language, animation and thematic games, and also elaboration of guidelines and booklets compiling the project main results.

3 Indoor and outdoor air quality evaluation

The air quality assessment in the town of Viseu was based in two experimental campaigns, one in winter (14–28 January 2006) and another in summer (19–26 June 2006). The measured parameters included ambient air concentrations of O_3, NO, NO_2, CO, SO_2, BTEX (benzene, toluene, ethylbenzene, xylene), PM_{10} and $PM_{2.5}$, measured continuously (in three mobile labs in winter and two in summer), using passive samplers and gravimetric methods, in different indoor and outdoor microenvironments. Additionally, numerical modelling simulations at mesoscale and local scale were performed.

3.1 Air quality measurements

3.1.1 Particulate matter

In the mobile laboratories installed in two schools, in urban and suburban location, PM_{10} concentrations were measured. In the urban school PM_{10} and $PM_{2.5}$ concentrations where measured in the outdoor and indoor (24 hour mean) by gravimetric methods, while in the suburban school only PM_{10} was measured. Figure 2 presents the PM concentration values measured in the winter campaign, where it can be seen that the PM_{10} values measured exceeded the limit value established in the Portuguese and European legislation (50 $\mu g.m^{-3}$) in some days of the experiments. The highest values were measured in the urban location.

Analysing the daily profile of PM_{10} concentrations it can be noticed that the peak concentrations are reached between 19:00 and 23:00. The PM_{10} values remain high during the night but decreasing until dawn. During daytime PM_{10}

values are lower with a local maximum at 11:00. In Viseu, biomass burning for residential heating is a common practice and is a possible source for the high values registered from 19:00 to 23:00. The similar behaviour of CO and SO_2 daily profiles, as well as the absence of these peaks in summer, reinforces this hypothesis. The measurements made in the classrooms show that the PM levels are very high. On weekdays, the PM_{10} concentrations in the classrooms are more than the double than in the outdoors of the same location. On weekends, the indoor PM values are similar to the ones measured in the outdoor, indicating the existence of indoor PM sources on weekdays.

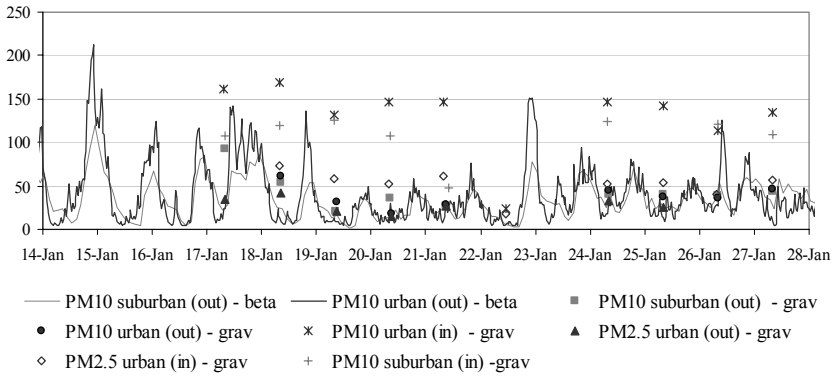

Figure 2: Particulate matter concentration values ($\mu g.m^{-3}$) measured in the winter campaign. beta – beta radiation; grav – gravimetric methods.

The PM outdoor values measured in the summer campaign are lower than in the winter campaign. Even though, the 24 hour averages are quite close to the limit value, and indoor concentrations are lower and closer to the outdoor values. This fact can be explained by the higher ventilation rates promoted by opening windows, a common practice during summertime.

3.1.2 Ozone and nitrogen oxides

During the two campaigns, O_3 and NO_x concentrations were measured continuously in the mobile laboratories and using passive samplers in 20 points distributed in the town of Viseu, in an area of approximately 40 km^2, and also in 44 indoor points (including children's houses and selected schools).

For the winter campaign, the NO_x and O_3 values continuously measured in the mobile labs did not exceed the limit values established in the legislation. During the summer campaign, the O_3 limit value for the protection of human health (120 $\mu g.m^{-3}$) was surpassed during three hours on the 21st of June on the suburban measurement location. Generally, the higher NO_x values were measured in the urban site, with the higher values corresponding to periods of higher traffic, while O_3 measurements were higher on the suburban location.

The representation of spatial distribution of NO_2 and O_3 concentrations obtained by passive sampling in winter and summer periods are presented in Figure 3.

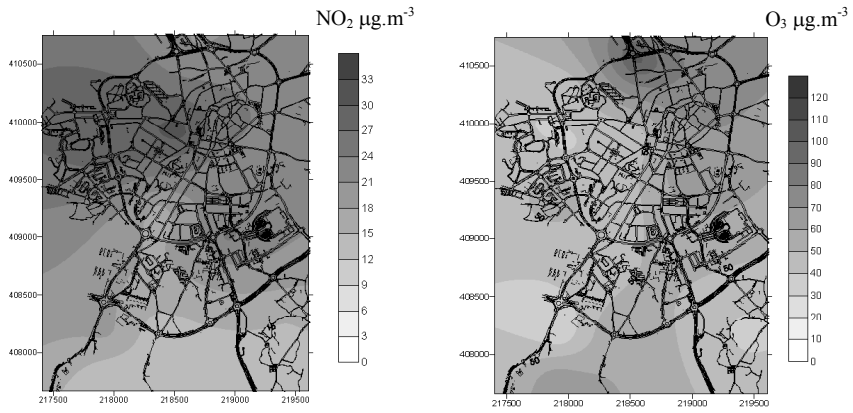

Figure 3: Spatial distribution over Viseu town, of NO_2 concentrations in the winter (left) and O_3 concentration in summer (right).

The results show that NO_2 highest concentrations occur in areas with greater road traffic. Ozone presents a different behaviour with low values in the location of higher NO_2 concentrations. Also, higher NO_2 concentrations occurred in winter campaign, reaching values of 33 $\mu g.m^{-3}$, in a week basis, while the O_3 remained quite low. In summer, the monitored concentrations of NO_2 decreased, but the week average of O_3 level increased to approximately 100 $\mu g.m^{-3}$.

Indoor concentrations of O_3 reveal ozone levels below 20 $\mu g.m^{-3}$. To evaluate the gradient of NO_2 concentrations between indoor and outdoor, ten values of NO_2 measured in houses were compared with nearby outdoor points, five located in the suburban area and other five situated in the urban area (Figure 4).

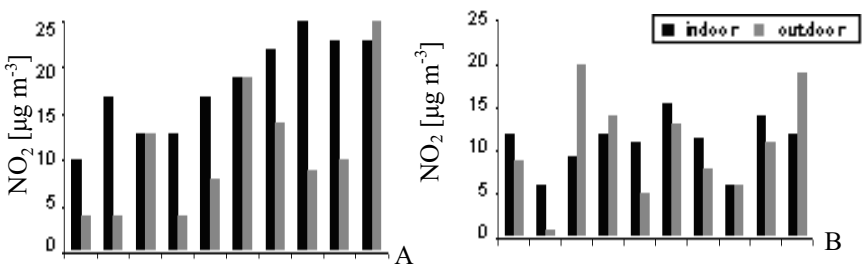

Figure 4: Relation between NO_2 indoor and outdoor concentrations in winter (a) and summer (b). The first five points are located in the suburban area and the last five are located in the urban area.

In general, NO_2 registered higher indoor concentrations in winter than in summer. Figure 4 shows also that the NO_2 gradient concentration between indoor

and outdoor is higher in winter; this can be explained by the presence of indoor sources, for example fireplaces are very common in this area, as well as by lower ventilation rates. Some bibliography identifies the use of domestic gas as a determinant indoor source of NO_2 [5, 6].

3.1.3 BTEX and formaldehyde

Formaldehyde and BTEX measurements were carried out for the schools (indoor and outdoor) and children's houses. The relations between indoor and outdoor concentrations of BTEX and formaldehyde were determined and are shown in Figures 5 and 6.

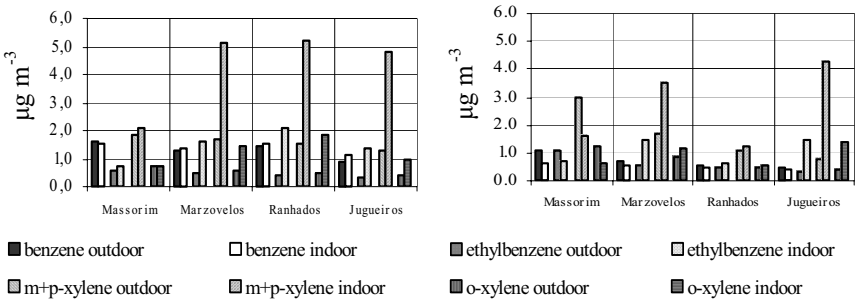

Figure 5: Concentrations of benzene, ethylbenzene, m-/p-xylene and o-xylene in winter (left) and in summer (right), measured indoor and outdoor of schools.

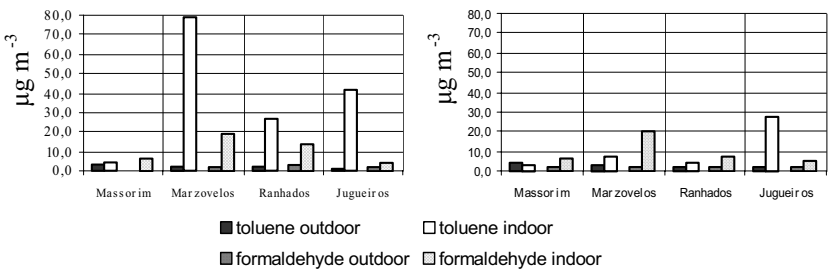

Figure 6: Concentrations of toluene and formaldehyde in winter (left) and in summer (right), measured indoor and outdoor of schools.

The concentration levels of the various organic pollutants have different behaviours. In winter indoor concentrations of toluene, formaldehyde, m-/p-/o-xylene and ethylbenzene are higher than those measured outdoor; in summer this situation is similar, with exception of measurements of toluene, m-/p-/o-xylene and ethylbenzene in the school of *Massorim*, where outdoor concentrations are higher. This situation reveals the significance of indoor sources for these

pollutants, such as particle board, insulation, furnishings, adhesives, solvents; in summer, the levels of measured indoor pollutants in schools appear to be lower than in winter, stressing the influence of ventilation rates in indoor air quality.

Benzene is the only organic compound which shows similar concentrations between indoor and outdoor measurements, pointing to the influence of outdoor sources in indoor air quality; also the benzene concentrations measurements were lower in summer. The threshold established for benzene (5 $\mu g.m^{-3}$ in EU Directive 2000/69/CE), was never exceeded in the schools measurements.

The results obtained in the children's houses revealed that 7% of the houses had benzene concentrations higher than 5 $\mu g.m^{-3}$. The concentrations of all pollutants tend to be lower in summer, with exception of formaldehyde, which shows a concentration increase; this behaviour was already described in other studies [7].

3.2 Air quality modelling

Two main objectives have been considered in the simulations: the models validation for the chosen domain and the study of the regional and local air pollution dispersion patterns. Considering the mesoscale simulations, emission database was built from the national emission inventory, using a top-down approach for the spatial and temporal desaggregation. At the local scale a bottom-up approach was applied to estimate the emissions from specific sources, such as traffic.

3.2.1 Mesoscale modelling results

The mesoscale modelling system MM5/CAMx was applied to characterise the spatial distribution of air pollutants concentrations. The MM5 is a non-hydrostatic meteorological model, with terrain-following coordinates, which simulates and predicts atmospheric circulations at the regional scale [8]. The CAMx, is an Eulerian photochemical model that simulates the emission, dispersion, chemical reaction and removal of pollutants in the troposphere over scales ranging from urban to regional [9]. A set of four nested domains was defined: Europe (27 km horizontal resolution); Portugal (9 km resolution); Central-North Portugal (3 km resolution) and Viseu (1 km resolution). CAMx was applied to the two smaller domains.

As an example, the spatial concentration fields for NO_2 obtained for the 17th January at 9:00 PM and O_3 obtained for the 20th June, for the smallest domain, are presented in Figure 7. As expected, higher NO_2 values are obtained at the city centre, while for O_3, a secondary pollutant, higher levels are reached outside the city as a result of the chemical reactions and pollutants transport. As long as for NO_2, the maximum concentration reached (70 $\mu g.m^{-3}$) is far from the legislated limit value, O_3 reaches values as high as 160 $\mu g.m^{-3}$, very close to the information threshold value (180 $\mu g.m^{-3}$). Although not shown, PM_{10} winter simulation results reveal high levels of this pollutant, exceeding the 50 $\mu g.m^{-3}$ daily limit value.

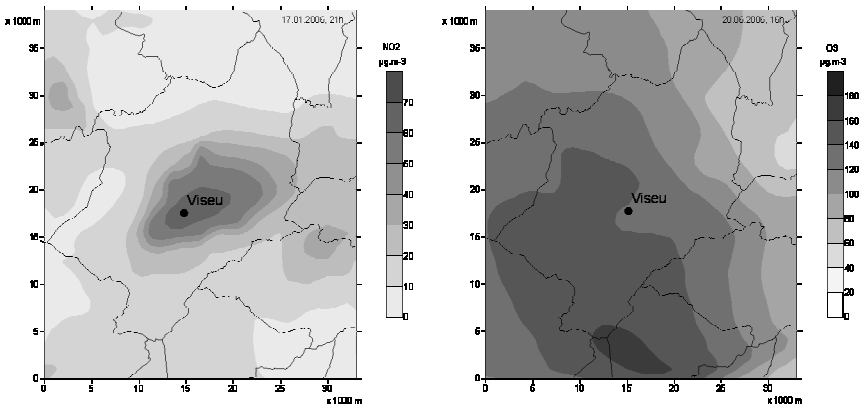

Figure 7: Mesoscale simulation results of NO_2 (17th January 2006, 21:00) and O_3 (20th June 2006, 16:00) surface concentration fields.

3.2.2 Local scale modelling results

Preliminary simulation at local scale was performed to calculate the dispersion patterns of NO_x from traffic, using the EPA Gaussian model ISCST3. The model was applied to an urban domain, with 3000x2000 m and grid resolution of 60 m, covering the area where the selected schools are located, and the period of 19th to 25th June. As input it was used the meteorological data measured in mobile laboratories during the campaign and a local station belonging to the Portuguese Meteorological Institute, and topography. Only traffic was considered, because is the most significant source of NO_x in this domain, and emissions were estimated using the traffic counts done during the campaign in the streets inside the domain and selected emission factors. The modelling results show low correlation with measurements, suggesting that other sources than traffic have to be considered.

4 Conclusions

Concerning this air quality evaluation in Viseu, results point that, with exception for particles, the other pollutants do not attain concentration levels of major concern. Particulate matter levels in Viseu are high, particularly in winter, which can be explained by the widespread use of biomass burning for residential heating. Also, inside classrooms and on weekdays, PM levels are very high. Further experiments are being done to assess this pollutant indoor sources in schools. Both outdoor and indoor concentrations are higher in the urban measuring sites.

The results show that the highest NO_2 levels are close to places with higher road traffic, while the O_3 concentrations are lower in these areas. The concentrations of O_3 are higher in summer than in winter, due to the higher temperatures monitored; as the ozone has its origin in photochemical reactions, has important seasonal fluctuations. From the measurements of NO_2, BTEX and formaldehyde was possible to understand that indoor sources are determinant in indoor air quality. The differences found between indoor and outdoor air quality

are due essentially to the type of activities, as well ventilation rate. The measured values were generally lower than threshold values, with exception of exceedences of benzene observed in 7% of houses.

The CAMx model presents reasonable simulation results when compared with the measured concentrations, namely identifying exceedances to the limit values. Additional work is planned for the local scale modelling, which needs to incorporate a more complete emissions inventory.

Acknowledgements

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Application of TAPM to predict photochemical air pollution over Portugal

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Abstract

The main objective of this paper is to study photochemical air pollution in Portugal through the application of the "The Air Pollution Model" (TAPM) (version 2.0), a 3D prognostic model that solves the fundamental fluid dynamics and scalar transport equations to predict both meteorology and air pollution concentrations. The possibility of using a meso-meteorological and dispersion model on an hourly base during an entire year represents an important achievement for air quality studies. The model was applied to Portugal, for the year 2003, to predict ozone concentrations. The simulation domain was 350 x 700 km with nested horizontal resolutions of 30 and 10 km. This domain included the entire Portuguese mainland and some of the surrounding ocean in order to adequately simulate the complexity of the atmospheric flow. Model predictions of meteorological surface parameters, such as wind and temperature, were compared with measurements of six meteorological monitoring sites. The Index of Agreement (IOA) was applied between observations and model results predicted on one year-long meteorological parameters. IOA is greater than 0.50 for all parameters, indicating a good agreement with measurements. Predicted ozone concentrations were compared with measurements from twelve air monitoring sites using the Paired Peak Estimation and the Median Bias Error. This numerical tool demonstrates a satisfactory performance to calculate mesoscale circulation patterns and photochemical air pollution over Portugal, providing important information to be used by decision-makers for air quality assessment.
Keywords: photochemical air pollution, mesoscale simulation, ozone.

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1 Introduction

Mesoscale circulations are phenomena sufficiently important for the photochemical simulation and its representation generally is made through meso-meteorological models capable to simulate the three-dimensional meteorological fields. Portugal is frequently under the influence of meso-meteorological circulations. The majority of the population and industry are located in the coastal area where sea breezes play an important role in the dispersion of atmospheric pollutants. In order to adequately study the circulation patterns of primary pollutants, as well as photochemical production it is necessary to simulate the atmospheric flow with mesocale models.

Most of air pollution dispersion models use semi-empirical or analytical approaches with input meteorological information typically derived from local surface-based observations. This meteorological information is not always available or has not sufficient detail, which can turn the application of these models very difficult. TAPM is an alternative 3D prognostic model that solves the fundamental fluid dynamics and scalar transport equations to predict meteorology and pollutant concentrations at local scale based on data obtained at global level. The approach followed by TAPM eliminates the need for specific meteorological data, while still offering the option of assimilating any observed meteorological data that might be available, and still simulates year-long periods with relative rapidity of calculation.

The possibility of using a meso-meteorological and dispersion model on an hourly base during an entire year represents an important achievement for air quality studies. The model was applied to Portugal, for the summer 2003, with the aim of predicting ozone concentrations.

2 Model description

TAPM is a three-dimensional prognostic model that solves the fundamental fluid dynamics and scalar transport equations to predict both meteorology and air pollution concentrations [1]. It uses global input databases of terrain height, land use, sea-surface temperature, and synoptic meteorological analyses. A complete description of TAPM version 2.0 and details of equations and parameterizations, including the numerical methods used to solve the model equations, can be found in [2] and [3], while a summary of some recent verification studies performed by CSIRO can be found in [4].

The meteorological component of TAPM predicts the local-scale flow, such as sea breezes and terrain induced circulations, given the larger scale synoptic meteorological fields. The model solves the momentum equations for horizontal wind components, the incompressible continuity equation for the vertical velocity in a terrain-following coordinate system, and scalar equations for potential virtual temperature, specific humidity of water vapour, cloud water and rain water. Pressure is determined from the sum of hydrostatic and optional non-hydrostatic components, and a Poisson equation is solved for the non-hydrostatic

component. Explicit cloud micro-physical processes are included. Wind observations can optionally be assimilated into the momentum equations as nudging terms. The turbulence closure terms in these mean equations use a gradient diffusion approach, including a counter-gradient term for the heat flux, with eddy diffusivity determined using prognostic equations for turbulence kinetic energy and eddy dissipation rate. A weighted vegetative canopy, soil and urban land-use scheme is used at the surface, while radiative fluxes, both at the surface and at upper levels, are also included. Boundary conditions for the turbulent fluxes are determined by Monin-Obukhov surface-layer scaling variables and parameterisations for stomatal resistance.

The air pollution component of TAPM uses the predicted meteorology and turbulence from the meteorological component, and consists of an Eulerian grid-based set of prognostic equations for pollutant concentration and an optional Lagrangean particle mode that can be used on the inner-most nest for pollution for selected point sources to allow a more detailed account of near-source effects, including gradual plume rise.

The chemical mechanism is based on the semi-empirical mechanism called the Generic Reaction Set (GRS) of Azzi *et al.* [5], with the hydrogen peroxide modification of Venkatram *et al*. [6]. In chemistry mode, there are ten reactions for thirteen species: smog reactivity (Rsmog), the radical pool (RP), hydrogen peroxide (H_2O_2), nitric oxide (NO), nitrogen dioxide (NO_2), ozone (O_3), sulphur dioxide (SO_2), stable non-gaseous organic carbon (SNGOC), stable gaseous nitrogen products (SGN), stable non-gaseous nitrogen products (SNGN), stable non gaseous sulphur products (SNGS), plus Airborne Particulate Matter (APM) and Fine Particulate Matter (FPM) that include secondary particulate concentrations consisting of (SNGOC),(SNGN), and (SNGS) [1].

3 Model application

TAPM was applied to the Continental region of Portugal, with a horizontal domain of 350 x 750 km, as shown in Figure 1, with nested resolutions of 30, 10 km and a vertical grid of 8000 m and 25 levels, with the first level 10 m above the ground. The model was applied for a period of 2 months from 1st of July 2003 to 31st of August 2003.

The Portuguese national air quality network used for validation of the modelling results includes many types of sites such as background, traffic and industrial monitoring stations, according to the criteria developed by the European Environment Agency. During the period selected for simulation only 12 monitoring stations, mainly concentrated in the coastal area, showed a consistent and feasible data.

The validation of the meteorological component was made with field data obtained in six meteorological stations distributed over the domain area. This analysis was developed for temperature, wind velocity and wind direction measured at 10 m above ground.

Locations of meteorological and air quality stations are shown in Figure 1.

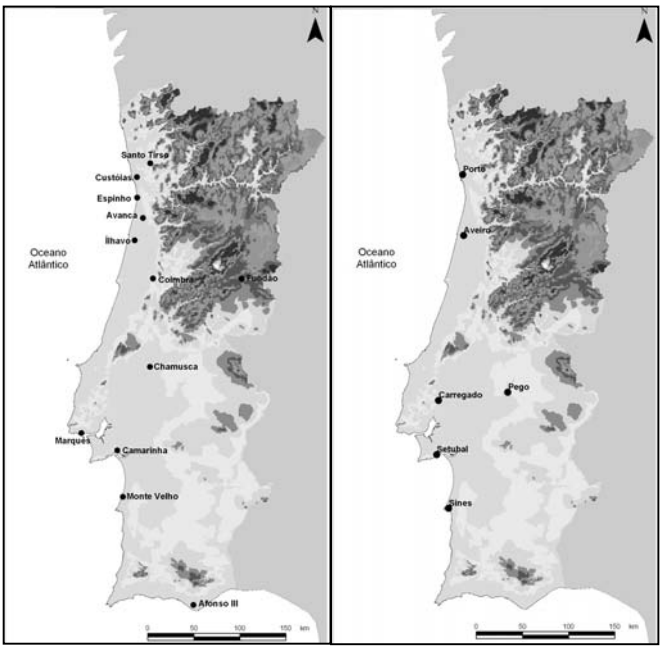

Figure 1: Simulated domain for Continental Portugal (350 x 750 km) with the location of air quality (left) and meteorology (right) monitoring sites.

3.1 Emissions

The area source annual emission data for NO_x, SO_2, CO and NMVOC were obtained from the Portuguese EMEP database [7] for the year 2001, for each pollutant activity (traffic, solvents, industrial and residential combustion and others).

These emissions were spatially disaggregated in order to obtain the resolution required, using adequate statistical indicators (types of fuel consumption and population census data) for each pollutant activity [8].

Annual emissions of large point sources were obtained directly from the available monitoring data of each industrial plant compiled on a database.

3.2 Meteorological episode

The meteorological episode was selected after the analysis of the ozone episodes measured in the national air quality network. Attention focused in the period between July and August 2003 that is considered as the most problematic in recent years for photochemical air pollution. In this 2003 there were 374 exceedances to the information threshold of ozone (180 $\mu g.m^{-3}$) between April and September with 256 exceedances only in August.

This period coincides with a major heat wave across much of Europe in the first two weeks of August 2003, during which temperatures peaked in August 1st, specially in the southern region of the country, with new records for the maximum of 47,3ºC in Amaraleja and for the minimum of 30,1ºC in Portalegre [9].

The Portuguese National Observatory of Health reported [9] an excess of 43% of deaths in Portugal for the period from 30th July to August 15th 2003 above the average for this time of year.

4 Results and discussion

4.1 Surface meteorology

Meteorological model predictions were extracted at the nearest grid point to each of the five meteorological monitoring sites on the 10 km grid spacing at 10 m above the ground for temperature and wind speed and direction. Statistics included the root mean square error (RMSE), the index of agreement (IOA) and the skill measurements ($SKILL_E$, $SKILL_V$, $SKILL_R$) and are based on the recommendations of Willmott [10]. The IOA is a measure of how well predicted variations about the observed mean are represented, with a value greater than about 0.50 considered to be good and 1 perfect. If the model shows skill the statistics $SKILL_V$ are near 1 and $SKILL_E$ and $SKILL_R$ must be less than 1. Table 1 includes the statistics of observations and model predictions for five meteorological monitoring sites.

Table 1: Statistics for the TAPM simulation for July to August 2003.

		Aveiro	Pego	Carregado	Setúbal	Sines
Wind speed	RMSE	2.45	1.56	3.48	7.47	1.76
	IOA	0.67	0.79	0.58	0.42	0.84
	$SKILL_E$	0.87	0.73	0.98	2.11	0.69
	SKILLV	0.89	0.93	0.88	0.90	0.98
	$SKILL_R$	1.20	0.86	1.56	3.06	0.77
west–east component (u)	RMSE	2.00	2.25	2.37	2.85	1.96
	IOA	0.79	0.87	0.68	0.56	0.89
	$SKILL_E$	0.88	0.51	1.02	1.57	0.62
	SKILLV	1.14	0.85	1.15	1.71	1.06
	$SKILL_R$	0.93	0.65	1.13	1.62	0.66
south–north component (v)	RMSE	2.06	2.32	2.70	3.68	1.95
	IOA	0.84	0.78	0.78	0.64	0.93
	$SKILL_E$	0.85	1.00	1.05	1.38	0.58
	SKILLV	1.27	1.38	1.40	1.63	1.09
	$SKILL_R$	0.86	1.06	1.08	1.45	0.55
Temperature	RMSE	6.90	3.75	3.52	5.47	2.67
	IOA	0.75	0.94	0.93	0.83	0.92
	$SKILL_E$	1.52	0.48	0.45	0.69	0.45
	SKILLV	1.18	0.99	0.91	0.85	0.93
	$SKILL_R$	1.43	0.51	0.52	0.84	0.54

These parameters indicate a reasonable performance of the model for the index of agreement (IOA). The IOA is greater than 0.50 for all parameters indicating therefore that a good adjustment exists between the estimated and

measured values. In the particular case of Setúbal, the lower values of IOA for wind speed can be justified by the insufficiency of data for this parameter on this particular meteorological station.

The comparison of the IOA determined for the meteorological parameters shows that in general, the IOA for the estimate of the temperature is better than the one obtained for the wind. This fact is expectable and confirms the good behavior of the radiative algorithm and land use parameterization of the model. The simulation of the atmospheric flow, analyzed through wind velocity and direction represents a phenomenon of bigger complexity resulting in a slightly lower value of IOA for these variables. The root mean square error values are lower than the standard deviations of the observations for most of the sites, indicating a high skill for the model. There are differences between the model and observed values of the wind components and speed, but these differences can be justified by insufficiency of data.

4.2 Ozone ground level concentrations

TAPM calculates ozone hourly average concentrations for the entire domain. Analysis of the modelling results was performed using time series, scatter plots and the calculation of the mean bias error (MBE) following a methodology used by EPA [11].

Figure 2 shows the spatial ozone concentration fields for July and August of 2003, in Portugal.

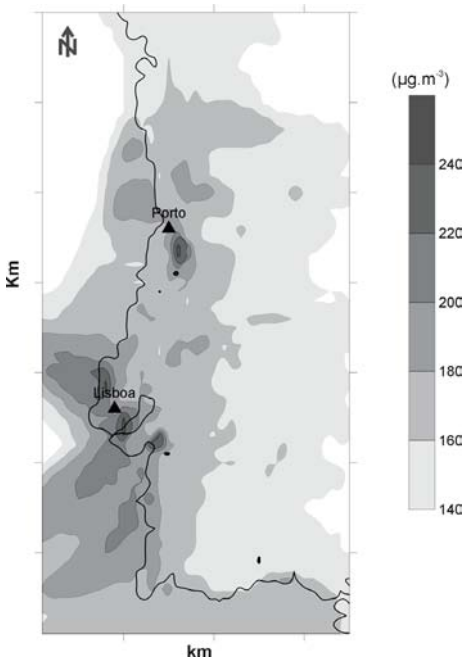

Figure 2: Maximum O_3 concentration fields for July and August of 2003.

According to modeling results, Ozone exceedances occurred during the simulated period, in large areas of Portugal where there were not any field data. Concentration patterns show that there is a potential advection and transport of the pollutants emitted from the major urban centers (Porto and Lisbon) to the coast and to some inland parts of Portugal. This scenario confirms other mesoscale meteorological simulations performed in this region by other authors [11–13].

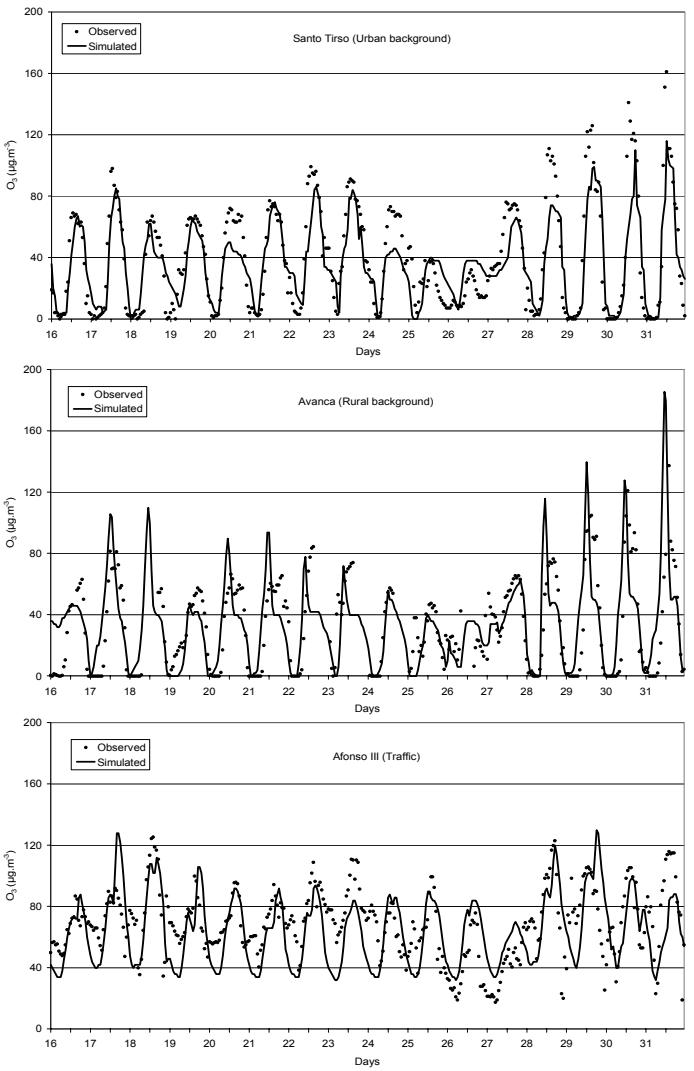

Figure 3: Observed and simulated hourly maximum ozone values for different types or air quality monitoring sites.

Figure 3 shows time series plots for a selection of three "representative" air quality monitoring sites, chosen to cover the different type of monitoring stations. The model is able to simulate the hourly maximum ozone variability and reproduces the episodic events of high ozone maximums as well as the interdaily variability.

The evaluation of the performance of the model is shown in Table 2. These results suggest that in these particular simulations the model has a tendency to underestimate the estimated values, in comparison with the measured data, since in 11 of the 12 sites the value of MBE is negative.

Table 2: Mean bias Error (MBE) for ozone.

Air Quality Site	MBE
Santo Tirso	-14
Custóias	-14
Espinho	-11
Avanca	6
Ílhavo	-25
Coimbra	-26
Fundão	-1
Chamusca	-2
Quinta Marquês	-29
Camarinha	-10
Monte Velho	-18
Afonso III	-10

5 Conclusions

TAPM was used to predict photochemical air pollution in Portugal, in July and August 2003. Model results were compared with data from national air and meteorological monitoring network. Results show that TAPM has predicted extreme concentration statistics for smog ozone in some sites but, in general, is able to simulate the hourly maximum ozone variability and reproduces the episodic events. The spatial ozone concentration shows that the pollutants emitted from Porto and Lisbon affects the coast and some inland parts of Portugal.

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Evaluating ozone spatial distribution in Portugal using passive samplers

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Abstract

Tropospheric ozone is a pollutant of major concern in Portugal and in Europe, especially during summer and spring time. In Portugal, several studies and the analysis of air quality data series highlighted high ozone (O_3) levels inland. A study was carried out to assess the rural background stations representativeness area for O_3. Monitoring campaigns were performed in the summer of 2005 within five Portuguese air quality management zones where critical levels are usually reached. O_3 passive samplers (148 diffusive tubes, one-week exposure) as well as a mobile monitoring station were used. In relation to spatial O_3 patterns, the studied air quality stations appear to be representative of the majority of their zones. Regarding the temporal representativeness, a trend was found for higher hourly O_3 correlations between sites located both on a coastal territory axis and on an inland territory axis. Thus, it seems that similar geographical, topographical and meteorological conditions are a more significant factor to define the stations area of representativeness, rather then the proximity between locations.
Keywords: ozone, representativeness, air quality monitoring stations, diffusive sampling.

1 Introduction

Ozone (O_3) is a secondary pollutant formed in the atmosphere as a result of reactions between primary pollutants (ozone precursors), such as, nitrogen oxides (NOx) and volatile organic compounds (VOC), emitted largely by industry and road traffic. Besides the O_3 formation processes there are also

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reactions promoting its destruction in a polluted atmosphere, by chemical titration with nitrogen monoxide (NO), in the nearby emission sources Airparif [1]. Thus, higher O_3 concentration values are not measured necessarily near the precursors emission sources but occur, downwind, in the surrounding areas, in a few tens of kilometres away Airaq [2]. O_3 is a photochemical pollutant reaching high concentrations especially during summer and spring time. The main meteorological variable that influences surface O_3 concentrations is the temperature although wind speed, ultra-violet radiation, atmospheric stability, atmospheric moisture and long-range transport could also have a significant role in ozone formation Comrie [3]. Forest fires can also play a significant role on O_3 generation, since VOC are released in the course of biomass combustion. Emissions from distant forest fires can contribute to regional accumulations of high O_3 concentrations McKeen *et al* [4]. Another relevant factor is the altitude effect, where an increase of O_3 levels is associated to a major photochemical production at higher altitudes Blankinship [5].

A monitoring station provides air quality data representative of a certain area around the station. According to the EUROAIRNET criteria the area in which the concentration does not differ from the concentration measured at the station by more than 20% is the area of representativeness of the station Larssen *et al* [6]. Passive sampling technique is frequently used to assess spatial distribution of air pollution, covering large areas, as Costabile *et al* [7] evidenced. Passive monitoring (by using diffusive samplers) combined with active monitoring (by using existing air quality monitoring stations and mobile units) is an approach that allows one to address the question of how representative the site and time period of air quality measurements actually can be Vardoulakis *et al* [8].

The third Daughter Directive 2002/3/EC on ozone in ambient air establishes an information threshold which means a level beyond which there is a risk to human health from brief exposure for particularly sensitive population and at which up-to-date information is necessary. In Portugal the air quality monitoring network, detects every year in summer and spring period some hundreds of exceedances to the information threshold, about 40% of them occur in the recently installed rural stations. Some of these stations registered the highest number of exceedances. Recent Portuguese studies demonstrate that high levels of O_3 affect more the inland territory rather than coastal areas. It was also been evidenced that orographycal characteristics, altitude, and the amount of solar radiation seemed to be correlated with the O_3 concentrations distribution (Ferreira *et al* [9], Mesquita *et al* [10]). The assessment of this stations area of representativeness, within the air quality management zones MAOT/DGA, UNL/FCT/DCEA [11] created in the context of the Air Quality Framework Directive, and the exposed population is for these reasons a major important issue in Portugal.

2 Methodology

The defined methodology for representativeness analysis was applied to the following zones and stations: Norte Interior zone (Lamas de Olo station), Centro

Interior zone (Fundão station), Vale do Tejo e Oeste zone (Chamusca station), Alentejo Interior zone (Terena station) and Algarve zone (Cerro station), which are represented in Figure 1.

The methods chosen to measure ozone concentrations were both passive and active sampling. As passive samplers, *Radiello* diffusive tubes were placed in 148 locations (about 30 per zone) in a grid of 20 km x 20 km in the vicinity of the station, and 40 km x 40 km within the zone. As active sampler, one mobile station equipped with an automatic analyser operating with a reference technique was placed in one location far from the fixed station in each zone during each campaign.

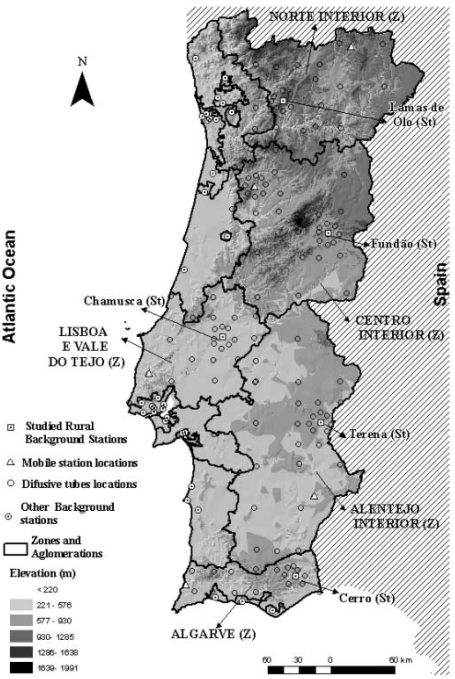

Figure 1: Delimitation of the Portuguese zones and agglomerations, and location of the studied rural stations, mobile station, diffusive sampling points and other national monitoring stations.

In terms of Quality Assurance/Quality Control (QA/QC) the procedures expressed in the Guidance Report on Preliminary Assessment EEA [12] for indicative measures were followed, and can be summarized as follows:

- keeping non exposed tubes in each campaign;
- expose several tubes in the same location (3 to 5) to evaluate the precision (repeatability of multiple measurements of the same event);
- expose several tubes in the fixed and mobile station location to evaluate the accuracy (truth of a measurement).

These procedures allowed the determination of uncertainty (degree of accuracy and precision of data) level of the campaign results.

Due to the financial, equipment, and time limitations, it was only performed a one-week campaign per zone, between 19-7-2005 and 14-9-2005. The chemical analysis of *Radiello* diffusive tubes were done in the Environment Reference National Laboratory, following the *Radiello* proceedings.

The data series analysis and interpretation included an uncertainty analysis for each campaign; mapping results obtained in each sampling spot and interpolation to obtain a continuous surface, using the Ordinary Kriging interpolation method (ArcGIS® 9.1 – extension Geostatistical Analyst); collecting ozone production related data: zones altimetry, meteorology during the campaigns and data on forest fires, to support the interpretation; and, evaluation of the area of representativeness of each station within the zone, according to the EUROAIRNET Criteria.

3 Results and discussion

The QA/QC evaluation included the analysis of precision, accuracy and uncertainty.

The level of repeatability of diffusive sampler measures can be evaluated through the coefficient of variation (CV), defined as the ratio of the standard deviation to the mean. A satisfactory CV, meaning low dispersion of results from samplers placed in the same site, would be less than 10% Garcia-Fouqué *et al* [13]. As it can be observed in Table 1, the CV didn't vary over 12% showing an acceptable precision.

In terms of accuracy levels, a good linearity of responses was obtained between the two monitoring methods, with a high coefficient of determination (R^2=91). The ozone concentrations measured by diffusive samplers exhibit a slight positive bias (over-read) in relation to those obtained by automatic analysers (from monitoring stations and the mobile unit).

Uncertainty is defined by the European Standard EN 13528-1:2002 (that specifies general performance requirements for diffusive samplers used for the determination of the concentration of gases in ambient air) as it follows, eqn (1):

$$\text{Uncertainty}\,(\%) = \frac{|\,x - x_{ref}\,| + 2S}{x_{ref}} \times 100 \tag{1}$$

where $\bar{x}$ represents the average of the passive samplers repeated measurements, x_{ref} is the value of the concentration measured by active monitoring, and S is the passive samplers repeated measurements standard deviation. When performing diffusive sampling campaigns a maximum measurements uncertainty of ±30% is proposed, as a data quality requirement EEA [12]. As presented in Table 1, considerable levels of uncertainty were obtained (from 16% to 46%).

The analysis of ozone concentrations, obtained in the five studied zones, and the information collected on factors influencing its chemistry, allowed to get a global picture of the conditions verified during the monitoring campaigns.

Table 1: Ozone concentrations measured by passive and active sampling ($\mu g/m^3$), at five Portuguese zones, standard deviation, coefficient of variation, and uncertainty associated to the passive sampling method

Zone	Location	Passive samplers			Active samplers	Uncertainty (%)
		Nr. samplers	O_3 ($\mu g/m^3$)	CV (%)	O_3 ($\mu g/m^3$)	
Norte Interior	OLO-AQMS	3	78	12	104	43
	VIN-MMU	2	92	0	79	16
Centro Interior	FUN-AQMS	5	63	12	59	32
	FORN-MMU	4	61	4	75	24
VTO	CHA-AQMS	3	77	7	74	18
	TUR-MMU	3	81	4	60	46
Alentejo Interior	TER-AQMS	3	66	6	51	46
	ENX-MMU	3	64	7	83	34
Algarve	CER-AQMS	3	130	5	100	43
	ALJ-MMU	2	124	5	102	33

CV- Coefficient of variation; VTO – Vale do Tejo e Oeste; AQMS – air quality monitoring station; MMU – mobile monitoring unit; OLO-Lamas de Olo; VIN-Vinhais; FUN-Fundão; FORN-Fornelo do Monte; CHA-Chamusca; TUR-Turcifal; TER-Terena; ENX-Enxoé; CER - Cerro; ALJ -Aljezur.

The Lamas de Olo monitoring station, located in the Norte Interior zone, registered the highest O_3 levels, and Terena monitoring station, sited in Alentejo Interior zone, recorded the lowest. The O_3 daily averages presented a high correlation with the maximum daily temperatures (77%, 69% and 68% in Vale do Tejo e Oeste, Norte Interior and Centro Interior zones). The lowest O_3 one-week average concentration was obtained for all monitoring stations during the Norte Interior and Centro Interior campaigns. Concerning passive monitoring the highest O_3 levels were measured in Algarve.

The 2005 summer had average temperatures (minimum, medium and maximum) higher than usual, and more than one heat wave were registered IM [14]. Had also been registered fires devastating a total of 3% of the Portuguese continental territory MADRP/DGRF [15]. In the period in which the Algarve and Alentejo campaigns were carried out MODIS satellite imagery allowed to observe the gas plume crossing the monitoring area, with possible influence on ozone chemistry.

The relationship between altitude of measurements and ozone concentration results was stronger in the Norte campaign (coefficient of determination R^2=50%). For the other studied zones the coefficients of determination varied from 22% to 46%, showing that, although altitude has some relation with ozone concentrations, there are other factors conditioning its levels.

Within respect to the temporal representativeness assessment a correlation matrix was produced for ozone hourly concentrations measured in all Portuguese rural background monitoring stations, from July, 1st to September, 30th 2005 (Table 2). Table 3 summarizes correlation coefficients obtained by comparing the ozone hourly concentrations measured in all rural background monitoring

stations with the mobile unit data sets, for each campaign period. Some general considerations about these results are as follows:

– stations from Norte Interior zone have a good level of common information (correlation coefficient of 78%), but in general are less correlated with stations from the other zones;

– stations from Centro zone are weakly correlated between them;

– stations from Vale do Tejo e Oeste, Centro Litoral and Alentejo Litoral zones, located near the Atlantic coast, are well correlated between them, and stations from the inland territory, as Fundão, Terena and Cerro also present good correlation levels;

– it seems that temporal correlation is stronger for locations across the country based on geographical characteristics such as inland/coastal features rather than the linear distance between measurement sites; an exception appears for stations located in Norte Interior and Centro zones, with specific characteristics in terms of elevations and slopes on land surface.

The analysis of representativeness for rural stations, within each zone, is represented in Figure 2. The ozone concentrations obtained by passive sampling, as points and areas, are presented in intervals of variation (in percentage) in relation to the rural station concentration. Table 4 provides additional information regarding the percentage of monitoring spots and areas that can be represented by the air quality station, and also a measure of spatial patterns error, obtained using geostatistics to interpolate sampling points measurements (Ordinary Kriging method).

Table 2: Correlation matrix of ozone hourly concentrations measured in all Portuguese rural background monitoring stations (from 1-7-2005 to 30-9-2005).

Zone		Norte L.	Norte I.	Centro L.	Centro I.	VTO	Alent. L.	Alent. I.	Alg.
	Station	MNH	OLO	ERV	FUN	CHA	MVE	TER	CER
Norte L.	MNH	1							
Norte I.	OLO	0,74	1						
Centro L.	ERV	0,54	0,45	1					
Centro I.	FUN	0,40	0,53	0,57	1				
VTO	CHA	0,67	0,58	0,73	0,62	1			
Alent. L.	MVE	0,44	0,37	0,74	0,62	0,71	1		
Alent. I.	TER	0,42	0,45	0,63	0,63	0,69	0,74	1	
Alg.	CER	0,55	0,59	0,53	0,63	0,70	0,61	0,70	1

L-Litoral; I-Interior; VTO-Vale do Tejo e Oeste; Alent-Alentejo; Alg-Algarve; MNH-Srª do Minho; OLO-Lamas de Olo; ERV-Ervedeira; FUN-Fundão; CHA-Chamusca; MVE-Monte Velho; TER-Terena; CER –Cerro;

Correlation coefficient (abslotute value): ☐ 0,30-0,50; ▒ 0,50-0,70; ■ >=0,70.

The area or points with a variation of less than 20% from the station concentration were considered within the area of representativeness of the station (EUROAIRNET criteria Larssen *et al* [6]). The results indicate that, during the campaigns periods, for all the zones in analysis, the respective rural stations are

representative of both the majority of rural points (between 61% and 75%) and practically all rural area within zones (between 70% and 100%). The higher percentage of representative areas in comparison with rural points is mainly due to the spatial modelling patterns that tend to smooth the points with concentrations not consistent with the neighbourhood. The maps also show that the distance from the station is not the most important factor to define the area of representativeness. The closest points are not always the most similar and well correlated. Other factors as territorial (land use and topography) and meteorological characteristics seem to have a more important role.

Table 3: Correlation coefficients of ozone hourly concentrations measured in all Portuguese rural background monitoring stations and in the mobile monitoring unit, for each campaign period.

Zone		Norte Int.	Centro Int.	VTO	Alent. Int.	Algarve
	MMU / AQMS	VIN	FORN	TUR	ENX	ALJ
Norte Int.	OLO	0,78	0,89	0,68	0,35	0,34
Norte Lit.	MNH	0,50	0,84	0,69	0,37	0,34
Centro Int.	FUN	0,70	0,50	0,61	0,81	0,35
Centro Lit.	ERV	0,57	0,61	0,80	0,64	0,50
VTO	CHA	0,74	0,89	0,66	0,67	0,73
Alent. Int.	TER	0,67	0,78	0,54	0,72	0,53
Alent. Lit.	MVE	0,68	0,65	NA	0,71	0,75
Algarve	CER	0,73	0,80	0,53	0,70	0,45

AQMS - Air Quality Monitoring Station; MMU - Mobile Monitoring Unit; Lit-Litoral; Int-Interior; Alnt-Alentejo; VTO-Vale do Tejo e Oeste; MNH-Srª do Minho; OLO-Lamas de Olo; ERV-Ervedeira; FUN-Fundão; CHA-Chamusca; MVE-Monte Velho; TER-Terena; CER - Cerro; VIN-Vinhais; FORN-Fornelo do Monte; TUR-Turcifal; ENX-Enxoé; ALJ –Aljezur; NA – Non available data for this period; Correlation coefficient within the same zone .

Table 4: Percentage of monitoring sampling sites represented by the station and areas of representativeness of each station (where the concentration variation regarding the station is less than 20%), and mapping error.

Zone	Station Location	Monitoring locations represented by the station (%)	Zone area represented by the station (%)	Mapping (ordinary kriging method) error (1)
Norte Int.	OLO	69%	90%	10%
Centro Int.	FUN	61%	100%	13%
VTO	CHA	67%	95%	13%
Alentejo Int.	TER	75%	77%	12%
Algarve	CER	64%	70%	10%

(1) Normalized Root Mean Squared Error= $(\Sigma(x_{Mod}-x_{Obs})^2)^{1/2}$ / Mean(x_{Obs}); Int-Interior; VTO-Vale do Tejo e Oeste; OLO-Lamas de Olo; FUN-Fundão; CHA-Chamusca; TER-Terena; CER-Cerro.

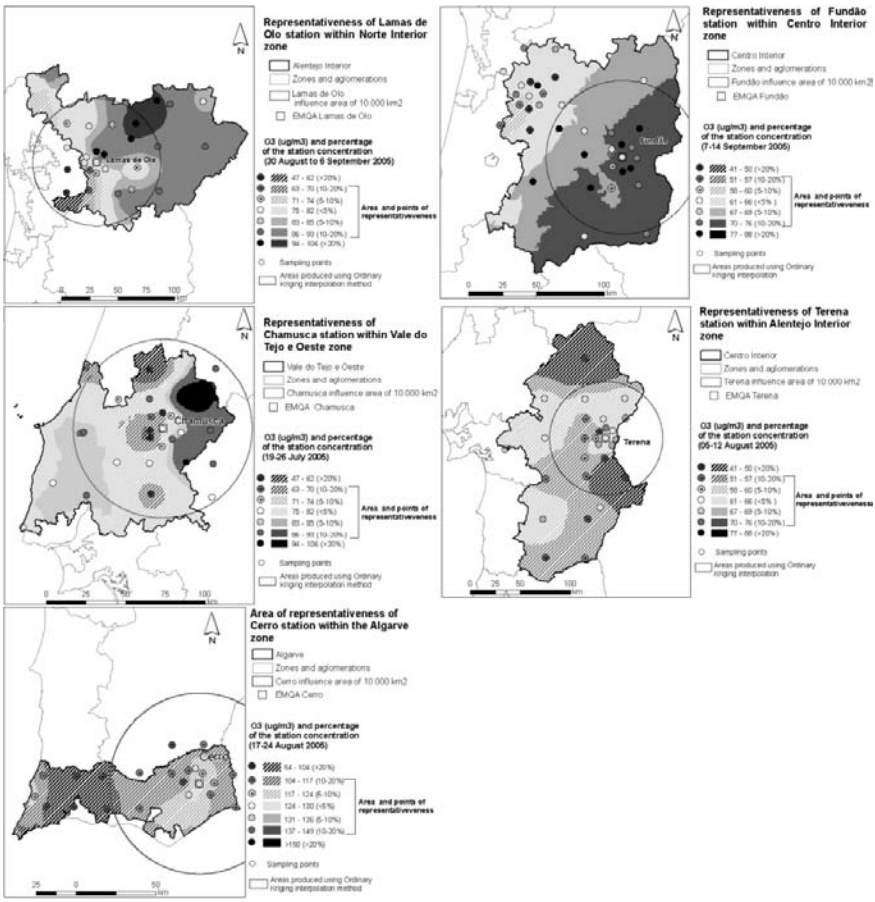

Figure 2: Area of representativeness of rural background stations within the zones in study.

In the analysis of these results one must take into account that for each zone only one week was measured, thus to obtain a more reliable picture the campaigns should be repeated covering at least 10% of the Summer and Spring periods (according to the ozone Daughter Directive 2002/3/EC).

4 Conclusions

A combination of passive monitoring (by using ozone diffusive samplers) and active monitoring (by using existing air quality monitoring stations and one mobile unit) has proved to be an efficient approach to address the question of how representative are the Portuguese rural background stations measurements.

The evaluation of the temporal representativeness was based on the hourly O_3 correlation matrixes gathered from a mobile monitoring unit and from rural

background monitoring network data sets. The results revealed higher temporal correlations between sites located inside a coastal territory axis and between sites located within an inland territory axis, showing that one important factor for temporal representativeness is sea proximity combined with orography.

Despite ozone concentrations obtained during these campaigns reflect a particular situation occurring in a specific period of time, air quality monitoring stations appear to be spatially representative of the great majority of each zone where they are located. This means that, for each studied zone, concentrations (obtained by interpolation of passive monitoring results) did not differ by more than 20% from the ones measured in rural background monitoring stations.

As a major finding of this study, it seems the proximity between sampling locations is not the most significant factor for the estimation of the area of representativeness for rural background stations. Geographical characteristics such as sea proximity, topographical features and meteorological conditions seem to be much better predictors for this end.

5 Future developments

A wider sampling period would be desirable in order to obtain more comprehensive data sets and a more reliable general picture of rural background air quality monitoring stations representativeness.

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Composition and source apportionment of atmospheric aerosols in Portugal during the 2003 summer intense forest fire period

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Abstract

The summer of 2003 was characterized by an intense heat wave across Europe that resulted in a large number of deaths and intense and extended forest fires. In Portugal, during this period more than 300000 ha of forests were destroyed by fire, during a short period, emitting enormous quantities of pollutants to the atmosphere. These emissions have presumably important effects in terms of regional human health and on the atmospheric radiation balance. During the summer of 2003 aerosol samples were taken in the Aveiro region, Portugal, and analysed for total mass and a series of inorganic and organic compounds, including tracers of biomass burning such as potassium and levoglucosan. Based on air mass trajectories, the aerosol size distribution, the levels of particulate mass and the aerosol composition, observed during periods with and without forest fires, the contribution of forest fires to the regional aerosol load is inferred. The absolute and relative variability of the aerosol inorganic and organic components are used to evaluate the importance of forest fire emissions as sources responsible for the presence in the summer atmosphere of compounds such as particulate tracers. The results permit also to have, at least, a semi quantitative estimation of the emission factors of biomass burning tracers such as potassium and levoglucosan to the organic aerosol load in air mass plumes resulting from forest fires. The calculation of emission factors from natural forest fires (without the bias of laboratory and prescribed burnings) is a useful complement for a correct inventory of the impact of these nowadays common summer events on the contamination of regional and global atmosphere.
Keywords: atmospheric aerosols, carbonaceous content, forest fires, levoglucosan, potassium.

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1 Introduction

Aerosols are minute particles suspended in the atmosphere. The major aerosol components include inorganic substances such as sulphates and carbonaceous species, which are divided into organic carbon (OC) and elemental carbon (EC). On a global basis, the major source of carbonaceous aerosols is biomass burning, due to forest fires and to the widespread use as fuel for heating homes and cooking [1–4]. Smoke aerosols perturb regional, and probably global, radiation budgets by their light-scattering effects and by their influence on cloud microphysical processes. Fine particles and the associated organic compounds are also of current apprehension because of their recognized health effects.

Substantial investigation on the contribution of biomass smoke to ambient aerosol levels has been executed for rain forests (e.g., [5–10]), smoked impacted areas in North America and Canada (e.g., [3, 4, 11–13]), and the aerosol outflow from the Asian continent (e.g., [14–16]). In Europe, data on detailed characterisation of atmospheric aerosols impacted by biomass burning are rather inexistent. Because of the specific weather conditions and the greater diversity of vegetation types burned in forest fires, regional differences in smoke impacted aerosol composition almost certainly exist. Accurate quantification of the amounts of particulate constituents emitted from forest fires and other sources of biomass burning on a regional and global basis is required by a number of users, including scientists studying a wide range of atmospheric processes, national governments who are required to report atmospheric emissions, and those interested quantifying the sources of air pollution that affect human health at regional scales.

In Portugal, it was estimated that, in the last decade, fires have destroyed around 110000 ha/year of forest, what corresponds to an annual loss of biomass of approximately 400000 ton [17]. Major forest fires raged across the country in 2003. Nearly 300000 ha of forest land were burnt, with cork and oak coverts particularly affected. The total area burned represented almost 5 times the average of the last two decades. The aerosol samples collected during the wildfire season of 2003 constituted an opportunity to evaluate the impact on background aerosol composition of emissions by extensive forest fires during drought conditions and a heat wave that has baked much of Europe for weeks.

2 Experimental

Integrated in the EU project CARBOSOL, during the summer of 2003, atmospheric aerosol samples were collected, continuously, on a weekly basis, on pre-fired quartz fibre filters. Aiming to separate particles into two size fractions (aerodynamic diameter, $dp<2.5$ μm and $2.5<dp<10$ μm), a $PM_{2.5}$ impactor (*Tisch TE – 231F*) and a PM_{10} size selective inlet (*Sierra SSI 1220*) were used. The sampling site was located in Moitinhos, Portugal (40º 35'N; 8º 38' W). It represented a rural area, situated 6 km southeast of the small coastal city of Aveiro with approximately 50000 inhabitants. The region is characterised by patches of maritime pine and eucalyptus mixed forests and by small scale

agricultural fields used for horticulture and maize growing. Filter samples were characterised at the University of Aveiro (carbon analyses), Laboratory of Glaciology in Grenoble (inorganic ions), University of Veszprem, Hungary (humic like substances – HULIS), and Technical University of Vienna (levoglucosan, cellulose and water soluble organic carbon – WSOC).

The carbonaceous content was analysed by means of home-made thermal-optical equipment [18, 19]. Controlled heating was performed to separate OC into four fractions of increasing volatility. The first fraction corresponds to the volatilisation at T<150ºC of lower molecular weight organics (OC1). Second and third fractions are related to decomposition and oxidation of higher molecular weight species at temperatures ranging from 150-350ºC (OC2) and 350-600ºC (OC3), respectively. The last fraction of OC is identified by transmitance and corresponds to pyrolised organic carbon.

The analytical procedure for the determination of cellulose in atmospheric aerosols was subdivided into three main steps: (i) an alkaline peroxide pre-treatment to improve the enzymatic accessibility by removing parts of hemicellulose and lignin; (ii) enzymatic conversion of cellulose to D-glucose and (ii) photometric detection of D-glucose [20]. The determination of levoglucosan and other sugars was performed by high performance liquid chromatography with an electrochemical detector [21]. For the determination of soluble potassium and its non-sea-salt and non-dust fraction, small parts of the filters were extracted with ultra pure Milli-Q water. The liquid extract was analysed for cations by ion chromatography with conductivity detection, using a Dionex 500 chromatograph. Determination of WSOC included soaking a spot of filter in Milli-Q water. The total carbon contents of the extracted filter spot were analysed by an Astro 2100 TOC analyser in the solid mode [22]. HULIS concentrations were determined by measuring the absorbance of the MilliQ water extracts with a UV-VIS spectrophotometer [25].

3 Results and discussion

3.1 Meteorological conditions, air quality and particulate carbonaceous content

The summer of 2003 was one of the hottest on record in Europe. In Portugal, the heat wave fanned the country's worst forest fires in more than 20 years. Air mass back-trajectories computed using the HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) model (not shown) indicate continental transport of the smoke from different inland regions of the Iberian Peninsula, depending on the days, to the western coastal sampling site of Moitinhos. Forest fires occurred, in particular, when the atmospheric circulation formed an important ridge associated with south-easterly conditions, and a strong advection of hot and dry air from northern Africa that was additionally heated when passing through central Iberia [24]. Meteorological results obtained for the Aveiro region over periods of large scale forest fires confirm an abrupt increase in the temperature, and a significant drop in the relative humidity records.

Between July 29 and August 13, all districts in Portugal experienced unusually high temperatures. At least 8 of the 18 mainland Portuguese districts had daily maximum temperatures above 32ºC during all this period. Four districts, corresponding to the non-coastal interior of Portugal, had daily maximum temperatures above 35ºC during the entire interlude (maximum temperature ever registered of 47.6ºC in Alentejo). This time interval, and several days after September 11 were the most affected by fire activity. During these episodes, in the Aveiro region, particulate matter levels were elevated 2- to 3-fold above the prior and post smoke baseline periods. However, PM_{10} hourly-averaged concentrations reached values higher than 300 μg m^{-3}, and even sporadic levels around 500 μg m^{-3} at some air quality monitoring stations closest to the forest fire fronts. The results show that the smoke layers and the reduced UV may have lowered the photochemical activity, reducing the ozone produced, during the first few days of the plumes' history (Figure 1).

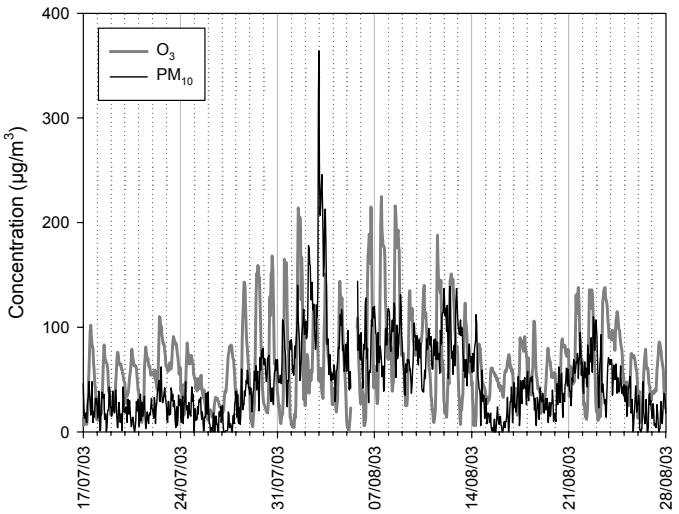

Figure 1: Particulate matter and ozone levels registered in the city of Coimbra, located about 50 km southeast of Moitinhos.

Average weekly $PM_{10}/PM_{2.5}$ ratios of 1.6 and 1.7 were obtained during the smoke events and for baseline periods before and after the fire episodes, respectively. Comparatively, Ward et al. [13] calculated a ratio of 1.3 during smoke events and of 2.4 for all other days throughout the summer of 2003 in Montana. A $PM_{10}/PM_{2.5}$ ratio of 1.7 was found in an airshed greatly impacted by residential wood burning with wintry conditions in Libby, Montana [25]. Ratios of 1.5 and 2.0 were measured in Seattle for the heating and non-heating seasons, respectively [26].

Elemental and organic carbon accounted for 17 to 39% of the $PM_{2.5}$ mass. The light-absorbing soot-like structures contributed to 12-26% of the carbonaceous material. Compounds that evaporate at lower temperatures

(<150ºC) represented 6-10% of OC, indicating that the contribution of semi volatile species to the organic particulate loading is small. Higher molecular weight species evolving above 350ºC in the thermograms constituted 12 to 21% of the OC mass. Pyrolised carbon dominated the OC fraction, signifying 52-63% of its mass (Figure 2). The carbonaceous content in the aerosol from Moitinhos is lower than values obtained with biomass burning aerosols over Amazonia (Graham [7]) and of the same range than levels measured in aerosol samples from the Lower Fraser Valley, Canada, impacted by forest fires [11]. Usually, more OC than EC is emitted by forest fires compared with other anthropogenic sources, resulting in a relatively higher OC/EC ratio during the smoke events.

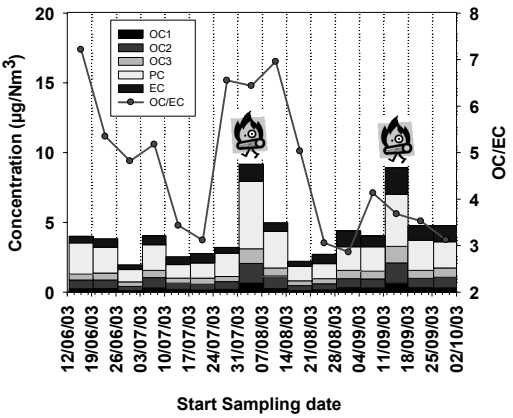

Figure 2: Variation of various carbon fractions and the ratio between organic and elemental carbon.

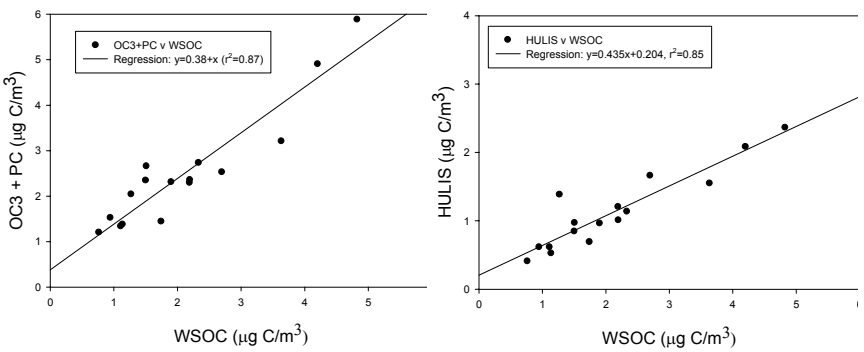

Figure 3: Linear correlations between OC fractions and water soluble organic compounds and between these and humic-like matter.

The WSOC content of the samples represented 43-83% of OC, which indicates the ability of the aerosol particles to act as cloud condensation nuclei and, as a consequence, influence cloudiness and climate. Its variation between

the biomass burning and cleaner periods is considerable, showing concentrations around 4-5 μg m^{-3} and less than 1 μg m^{-3}, respectively. The good correlation between the heavier molecular weight fraction plus pyrolised carbon (OC3+PC) and WSOC (Figure 3) suggests that the biomass burning aerosol was mainly affected by flaming combustion, which may also have contributed to the water soluble refractory matter (soluble fraction of HULIS).

3.2 Anhydrosugars and potassium

Three anhydrosugars (levoglucosan, mannosan and galactosan) were identified in the aerosol samples. Levoglucosan and the related degradation products from cellulose can be utilised as specific and general indicator compounds for the presence of emissions from biomass burning in samples of atmospheric fine particulate matter [27]. These compounds accounted for 1.1-4.0% and 1.3-6.5% of OC and WSOC, respectively. As expected, the anhydrosugars were confined chiefly to the fine fraction, since smoke aerosol consists, for the most part, of accumulation mode particles. Levoglucosan presented levels between a minimum of 17 ng m^{-3} and an upper limit of 105 ng m^{-3}, which was achieved during a vast wildfire period. Much higher average levels of 1200 and 2500 ng m^{-3} have been reported for forest and pasture sites, respectively, in 1999, during the burning season in Rôndonia (southwest Amazonia) [7]. Cellulose itself experienced an augment in concentrations during the periods of increased smoke plumes, while a slight drop of its contribution to OC is observed at the same time (Figure 4). Cellulose decomposes on heating or on exposure to an ignition source, giving rise to diverse breakdown products [27].

Based on the average value between the OC/levoglucosan ratio of 12.3 measured for the fine dry season aerosol in Rôndonia [7] and the ratio of 10.5 obtained for a pine forest fire in southeast USA [28], a smaller than expected contribution (11-36%) of wood combustion to the amount of OC throughout the summer CARBOSOL campaign (Figure 5). Thus, unrealistically, its seems that the major fraction of OC measured in both fine and coarse aerosols during the present study was chiefly related to other primary anthropogenic and biogenic sources, as well secondary formation processes. In spite of a significant raise in OC levels during the two weeks with strongest impact from the forest fire smoke plumes, the levoglucosan concentrations and the estimated contribution of wood burning to OC did not increase as expected. However, if the average levels of OC and levoglucosan measured during the 3 weeks less affected by wildfires are taken as baseline values and if these values are subtracted from the corresponding concentrations during the intense forest fire periods, then an OC/levoglucosan ratio of 80 is obtained. This analysis make evident that the OC/levoglucosan relationships proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols should be taken with precaution. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific factors with application to wildfires under extreme weather conditions (dryness and high temperatures) in Mediterranean countries.

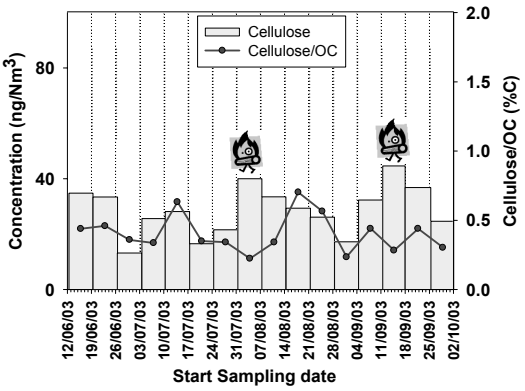

Figure 4: Concentrations of cellulose and its contribution to OC levels in atmospheric aerosols.

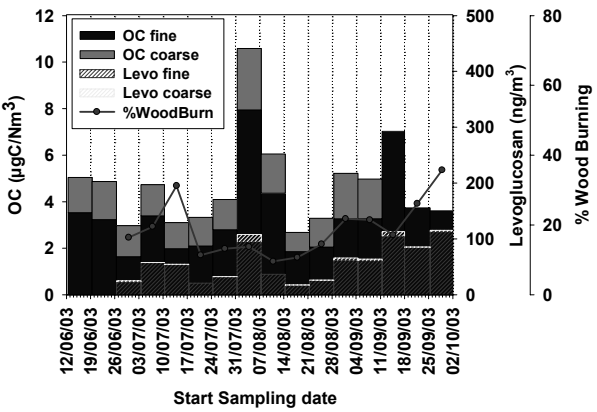

Figure 5: Variation of organic carbon and levoglucosan concentrations in both the fine and coarse aerosol fractions and contribution of smoke particles to the OC content.

It should also be mentioned that the emission of particulate matter constituents is quite different during the main combustion phases: flaming and smoldering [29, 30]. During smoldering combustion or in the initial thermal decomposition large quantities of levoglucosan are formed. During the flaming phase at higher temperatures (>400°C) levoglucosan re-polymerizes into polysaccharides, which then further react to form organic solids containing conjugated double bonds and carbonyl groups, as can be found in HULIS [31]. Another possibility is that some or all the HULIS is just humic matter from soil and/or putrefying leaf litter lofted during combustion [8]. Significant correlations between both HULIS fractions and biomass combustion tracers support the

hypothesis of biomass combustion emissions as precursors for a sizeable fraction of atmospheric HULIS in aerosols from Moitinhos.

Potassium is an important major emission from biomass burning [32]. The fraction of soluble potassium not related to sea-salt and soil dust (Knssnd) has been used as a qualitative tracer for biomass combustion [33]. The Knssnd was estimated by subtracting, from the soluble potassium determined on bulk aerosol filters, the sea-salt contribution, considering the mass ratio of potassium to sodium in seawater (0.038) and the marine sodium levels [34]. Since the dust material contains leachable potassium, its contribution was also subtracted by using non sea-salt calcium levels and assuming a mean K/Ca ratio of 0.36, which corresponds to the minimum value obtained over a year long period of measurements in the Aveiro region. Based on this estimation, it was found that the fraction of soluble potassium not related to sea-salt and soil dust constituted 38%-85% of the total. The modest correlation between the levoglucosan and Knssnd (r^2=0.37) and K/levoglucosan ratios up to several units are indicative of additional potassium inputs from other sources. It should be remembered that typical K/levoglucosan ratios reported in the literature for different types of biomass combustion do not exceed 0.5 [21, and references therein]. However, higher relationships have been observed by Schkolnik et al. [30] during a biomass burning experiment in Rôndonia. These researchers attributed the higher values to a more extensive oxidation during the biomass burning process. It is also probable that an important part of the potassium found in our atmospheric aerosol derive from soil lofted during combustion. This hypothesis is corroborated by the parallel increment in concentrations of potassium and calcium (a crystal trace element) during forest fires events (Figure 6) and a clear positive correlation between them.

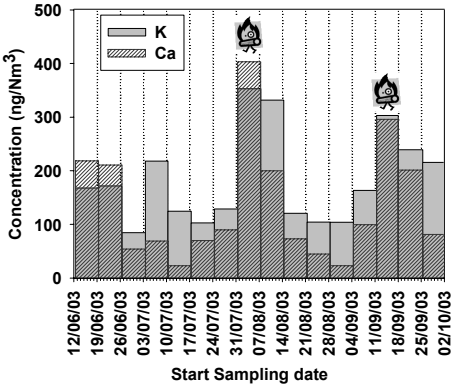

Figure 6: Summer variation in concentrations of potassium and calcium detected in atmospheric aerosols.

3.3 Sugars and sugar alcohols

Total sugar alcohol and monosugar concentrations ranged from about 40 to 100 ng m^{-3} with maximum level found in a sample less affected by the passage

of the smoke plume from the forest fires. The majority of the sugar polyols identified (arabitol, sorbitol and mannitol) were found to be most prevalent in the coarse fraction. Saccharide alcohols are known components of bacteria, fungi, lichens, invertebrates and lower plants, acting as osmoregulators, stress inhibitors or carbohydrate suppliers [12, 35]. A general lack of correlation with various biomass burning tracers and higher coarse fraction concentrations were taken as indication that these compounds may be part of the natural background aerosol with a likely association with the primary biological particles. An exception should be referred for xylitol, which presented a fine/coarse ratio between 2 and 4 during the weeks of intense forest fires, inverting the proportion over periods with less influence of smoke.

The dominant primary monosaccharides in aerosols from Moitinhos are comprised of glucose, mannose, fructose, arabinose, with minor quantities of galactose. There are several sources of these constituents, including microrganisms, vascular plants and animals [12]. Simoneit et al. [36] suggested soil and associated microbiota as the main source of saccharides to the atmosphere. According to these researchers, all these compounds derive mainly from soil resuspension into the atmosphere, though emissions of considerable amounts may occur by thermal stripping during biomass burning events. Contrarily to the majority of sugar alcohols, the monosaccharide constituents presented higher fine fraction concentrations and a moderate correlation (r^2=0.42-075) with levoglucosan. The proportion between the fine and the coarse fraction increases during periods of severe forest fires, indicating and origin from biomass burning. This observation is in accordance with the results presented by Medeiros et al. [12], who registered enrichments by factors of 2-5 in samples collected under the influence of smoke plumes from Quebec forest burning, indicating that wildfires also enhances emissions of uncombusted saccharides. Moreover, good correlations were generally obtained between pairs of sugars within each group, suggesting a common origin. Xylitol constitutes an exception, since it is better correlated with monosaccharides than with other polyols. Thus, microbiota or other primary biological sources may have not contributed to the observed xylitol levels, resulting probably from the forest fire emissions. Curiously, an investigation by Simoneit et al. [36] of the saccharide content of various representative agricultural soils and both paved and unpaved road dusts revealed that glucose was a dominant constituent in samples of all types, while xylitol was only detected in some samples of paved road dust, indicating a different origin than its relative compounds.

4 Conclusions

During the wildfire episodes, in the Aveiro region, particulate matter levels were elevated 2- to 3-fold above the prior and post smoke baseline periods. The carbonaceous material accounted for 17 to 39% of the $PM_{2.5}$ mass and was noticeably represented by high molecular weight organic matter. Evidence of biomass burning as a significant source is supported by the presence of anhydrosugars and potassium in atmospheric aerosols. On the basis of typical

OC/levoglucosan ratios reported in the literature, it was estimated that smoke particles accounted for 11-36% of the OC content, manifesting a smaller than expected impact. The OC/levoglucosan relationships proposed in the literature for deriving the amount of OC from wood or biomass combustion in ambient aerosols should be taken with precaution. Since the ratios are quite variable for different burning conditions and wood types, it has yet to be estimated more specific factors with application to wildfires under extreme weather conditions in Mediterranean countries. Identical conclusion is achieved when using typical K/levoglucosan ratios. It is probable that part of the potassium (and other elements) found in atmospheric aerosols derives from soil lofted under extreme combustion conditions.

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Influence of traffic on the elemental composition of PM_{10} and $PM_{2.5}$ in Oporto region

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Abstract

The aim of this work was to study the influence of traffic emissions on the physical and chemical characteristics of PM_{10} and $PM_{2.5}$, namely considering: concentration, size distribution and elemental composition. Four monitoring sites in the north of Portugal were selected: two sites directly influenced by traffic emissions and two rural background sites. PM_{10} and $PM_{2.5}$ samples were collected using low-volume samplers; the element analyses were performed by particle induced X-ray emission (PIXE). At the sites influenced by traffic emissions PM_{10} and $PM_{2.5}$ concentrations were 7-9 and 6-7 times higher than at the background sites. The presence of 17 elements (Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb) was determined in both PM fractions; particle metal contents were 3-44 and 3-27 times higher for PM_{10} and $PM_{2.5}$, respectively, than at the backgrounds sites. The results also showed that in coastal areas sea salt sprays are important sources of particles, influencing PM concentration and distributions (PM_{10} increased by 46%, $PM_{2.5}/PM_{10}$ decreased by 26%), as well as PM compositions (Cl in PM_{10} was 11 times higher).
Keywords: air pollution, particulate matter, traffic emissions, PM_{10}, $PM_{2.5}$, PIXE, metallic composition, Portugal.

1 Introduction

Many European countries are nowadays concerned with the numerous negative effects of traffic. During the past 3 decades the motor vehicle traffic has been massively increasing: between 1970 and 1995 the use of cars in Europe Union doubled. The consequences of traffic have been well recognized: injuries, traffic

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noise, effects on metal health and wellbeing, and more importantly air pollution. Special efforts have been made during last two decades, aiming the reduction of adverse impacts of air pollution, despite that, air pollution in Europe is still a matter of concern, mainly related with impacts on the human health and on the environment. The levels and composition of traffic related pollutants in air depend on several factors such as the number of vehicles, types of used fuels, type and conditions of engines, type of environment and meteorological conditions; however, ozone (O_3), nitrogen oxides (NO_x), carbon monoxide (CO) are considered as the most serious traffic-related air pollutants, among them particulate matter (PM) being one of the most important.

In Europe, exhaust from motor vehicles is considered to contribute more than 50% for emission of PM_{10} (particles with aerodynamic diameter smaller than 10 μm) (Kunzli *et al* [1]). Previous research has mostly focused on vehicle exhaust particulate emissions, because it was generally assumed that fuel combustion was the primary mechanism by which the particles were formed (Sagebiel *et al* [2], Kleeman *et al* [3]). Nevertheless, tire, brake and clutch emissions, and resuspended dust also contribute to atmospheric particulate matter Mulawa *et al* [4].

PM has been intensively studied within many epidemiological studies in Europe and North America Dockery and Pope [5], Brunekreef and Holgate [6], Hoek *et al* [7], Alvim-Ferraz *et al* [8]. Those studies showed the association between the increase of ambient concentrations of PM_{10} (that can penetrate the respiratory tract) and especially $PM_{2.5}$ (particles with aerodynamic diameter smaller than 2.5 μm that can penetrate in the deeper parts of the lungs) and the increase of morbidity and mortality rates, caused by pulmonary and cardiovascular diseases; the smaller the particles, the more evident the health effects Kaiser [9].

Despite the enormous number of epidemiological studies, there is a remaining uncertainty, if it is the physical (namely size and shape) or the chemical PM characteristics that have the most important role on the adverse health effects. A typical sample of PM consists of several chemical substances among them crustal compounds, minerals and trace metallic elements (Harrison *et al* [10], Sondreal *et al* [11], Tripathi *et al* [12], Sharma *et al* [13]). Some of the trace metallic elements present in PM (As, Cd, Co, Cu, Hg, Mn, Ni, and Pb) are human or animal carcinogens (Manalis *et al* [14]), therefore EU has stressed the importance of this subject setting the Directive 2004/107/EC that defines target values and assessment thresholds of arsenic, cadmium, mercury, nickel and PAH (benzo(a)pyrene) in PM_{10}, requiring the respective long-term assessment. Nevertheless, the knowledge about the impact of PM metallic composition on health is still scarce, which justifies an increasing effort concerning the characterization of the metallic composition of smaller fractions of PM.

Many of the epidemiological studies related to PM consider only PM_{10}. Nevertheless, as most of the PM traffic emissions are in the fine fraction, more information on $PM_{2.5}$ should be provided namely concerning the levels and elemental composition, as the actual knowledge is still scarce on that. Thus, considering the relevance of that knowledge for a further evaluation of the

influence of traffic emission on public health, the work developed included the detailed characterization of PM_{10} and $PM_{2.5}$, sampled at sites directly influenced by traffic, as well as at reference sites. Bulk elemental composition of PM was determined by particle induced X-ray emission (PIXE). The specific objectives were to study the influence of traffic emission on PM_{10} and $PM_{2.5}$ characteristics, considering: (1) concentration and size distribution; and (2) bulk elemental composition.

2 Methods

Monitoring of PM_{10} and $PM_{2.5}$ was performed in the north of Portugal during winter and spring of 2005 at four sites: two directly influenced by traffic (Tr_1 and Tr_2) and two not directly influenced by anthropogenic emission (background Bc_1 and Bc_2). Sampling was performed for 21 consecutive days at sites Tr_1 and Tr_2, and for 10 and 22 consecutive days at sites Bc_1 and Bc_2, respectively.

Both the traffic sites were situated at a zone of Oporto (Paranhos district), where several public institutions, high and secondary schools, and universities are located. The area is near one of the most important access points to the highway and the traffic emissions are the main source of atmospheric pollutants (Salcedo *et al* [15], Pereira *et al* [16]). Site Tr_1 was situated about 30 m west from the highway while site Tr_2 was located at the car park entrance of one of the universities, at about 50 m east from one of the main streets.

Site Bc_1 was situated in the natural park of Alvão, located in the northern interior lands of Portugal, approximately 115 km east from Oporto. Site Bc_2 was situated approximately 13 km far from seacoast in a remote area, about 112 km north from Oporto city. Based on given classifications (Larssen *et al* [17]), both Bc_1 and Bc_2 were considered as rural (regional) background sites. The locations of all sites are shown at Figure 1.

The sampling equipment worked every day from 8.00 a.m. to 8.00 p.m. to perform monitoring periods of 12 hours. Such a period was chosen in order not to over-load filters for consequent chemical analysis. The collection of the different PM fractions was done using TCR TECORA Bravo H2 constant flow samplers, combined with PM_{10} and $PM_{2.5}$ EN LVS sampling heads in compliance with the norm EN12341. A sampling air flow rate of 38.3 L min^{-1} was applied. The particles were collected on polytetrafluoroethylene (PTFE) membrane filters with polymethylpentene support ring (2 μm porosity, Pall Life Science Teflo™).

PM masses were determined gravimetrically by subtracting the initial average mass of the blank filter from the final average mass of the sampled filter; the difference was then divided by the total volume of air passed through filter (at 25ºC and 101.3 kPa). The steps of pre- and post-sampling gravimetric mass determinations were the following: 24 h to equilibrate filters before weighing at room temperature (Mettler Toledo AG245 analytical balance weighing with accuracy of 50 μg) followed by weighing during the following 24-48 h. If the measurements for one sample differed more than 50 μg, they were discarded and the filters were repeatedly weighed until three reproducible values were

obtained. For the data treatment, the Student's t-test was applied to determine the statistical significance ($P<0.05$, two tailed) of the differences between the averages determined for all the sites. For elemental analysis the filters were cut in half. One half was analysed by particle induced X-ray emission (PIXE) while the other part was kept for possible replicates and other analysis. The PIXE analysis used a beam of 2.150 MV without a filter.

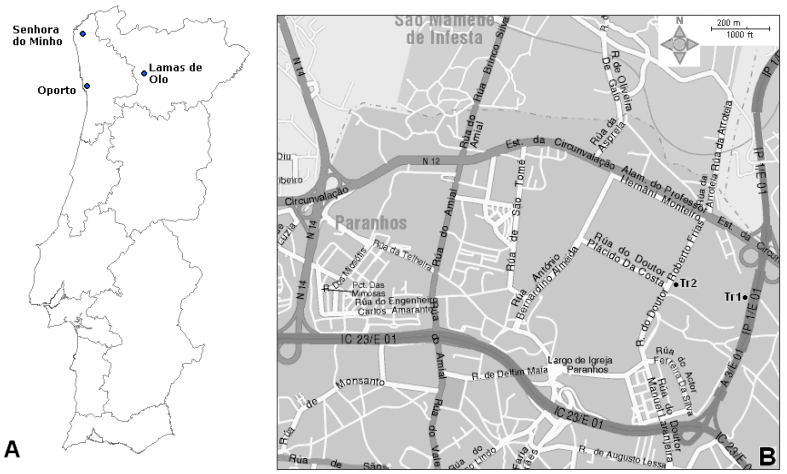

Figure 1: Monitoring sites: A) in Portugal B) in Paranhos district.

3 Results and discussion

3.1 PM_{10} and $PM_{2.5}$ concentrations

The means as well as other statistical parameters of PM_{10} and $PM_{2.5}$ measured at the two sites influenced by traffic emissions and at the two background sites are shown in Figure 2. The statistical analysis of these results indicated that: i) PM_{10} and $PM_{2.5}$ concentrations were significantly lower at the background sites than at the traffic ones; ii) the differences observed between PM_{10} means (as well as between $PM_{2.5}$ means) at Tr_1 and Tr_2 were not statically significant; iii) PM_{10} and $PM_{2.5}$ means were not significantly different at sites Tr_1, Bc_1 and Bc_2, demonstrating that most of PM_{10} fraction was composed by $PM_{2.5}$; and iv) PM_{10} means at Bc_1 and Bc_2 were significantly different, while no difference was observed for $PM_{2.5}$. In addition, it was found that at both Tr_1 and Tr_2 PM_{10} concentrations were well correlated with $PM_{2.5}$ as the correlation coefficient square (R^2) is 0.92 (Figure 3), indicating that PM_{10} and $PM_{2.5}$ at these sites were influenced by similar sources. In general, the results showed that traffic emissions increased about 7-9 times PM_{10} concentrations and about 6-7 times $PM_{2.5}$ concentrations.

To study the association between both PM fractions, the $PM_{2.5}/PM_{10}$ ratios were analyzed with more detail. The $PM_{2.5}/PM_{10}$ ratios were calculated from

each measurement and the means of $PM_{2.5}/PM_{10}$ as well as other statistical parameters are shown in Table 1.

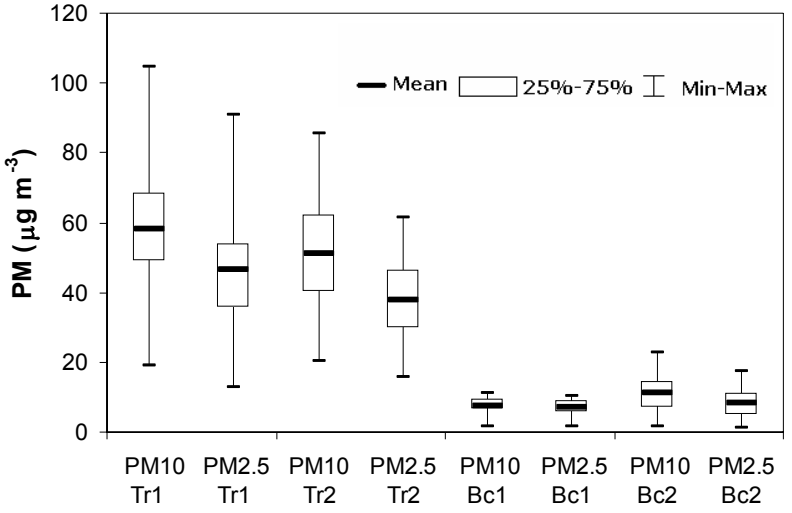

Figure 2: Atmospheric concentrations of PM_{10} and $PM_{2.5}$ measured at the four sites in Portugal: means, minima (Min) and maxima (Max) values, 25th and 75th percentiles.

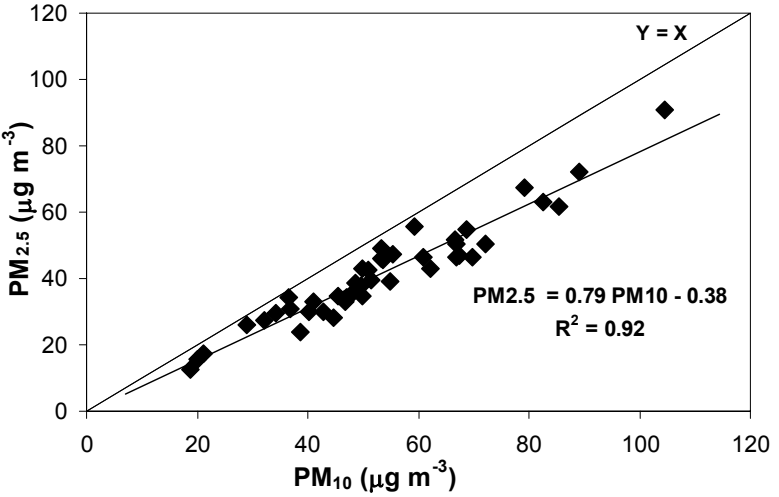

Figure 3: $PM_{2.5}$ and PM_{10} correlation for the traffic sites.

During the monitoring campaigns the differences observed between the means of the ratios at both traffic sites and Bc_2 were not statistically significant; however, $PM_{2.5}/PM_{10}$ ratios were slightly higher at sites Tr_1 and Tr_2. The mean

ratio obtained at site Bc_2 (0.72) was the lowest of all sites. As mentioned previously, site Bc_2 was located close to the seacoast. Sea salt sprays are mainly composed by coarse particles which justified the lower values observed for $PM_{2.5}/PM_{10}$. This conclusion was also supported by the comparison of particle levels (Figure 2). The means of PM_{10} were significantly lower at Bc_1 (distant from the seacoast) than at Bc_2 (close to the seacoast); nevertheless, $PM_{2.5}$ concentrations were not significantly different. Thus, the obtained result showed that sea salt spray plays an important role as particle source in coastal areas of Portugal and its contribution to PM_{10} particle distributions should be assessed. The highest mean ratio (0.91) was observed at site Bc_1. This value indicates that background PM_{10} was mostly composed of fine particles. At this moment, discussions among the scientific community suggest the implementation of $PM_{2.5}$ air quality standards, which could in the future replace present PM_{10} standards. As sites with similar characteristics in other European countries showed lower $PM_{2.5}/PM_{10}$ ratios (Van Dingenen *et al* [18]), the accomplishment of new $PM_{2.5}$ limits in Portugal might be more difficult than in other regions. As $PM_{2.5}$ have strong influence on lung diseases (Maynard and Howard [19]), information about high $PM_{2.5}/PM_{10}$ in Portugal is also relevant for the development of strategies to protect public health.

Table 1: Statistics for $PM_{2.5}/PM_{10}$ ratios at the four sites.

Site	$\frac{PM_{2.5}}{PM_{10}}$ mean	SD	Min	Max	25th percentile	Median	75th percentile
Tr_1	0.79	0.07	0.67	0.92	0.76	0.78	0.83
Tr_2	0.75	0.07	0.62	0.86	0.70	0.74	0.80
Bc_1	0.91	0.05	0.83	0.99	0.88	0.91	0.96
Bc_2	0.72	0.15	0.41	0.94	0.64	0.77	0.81

3.2 PM_{10} and $PM_{2.5}$ bulk elemental compositions

The emissions of particles related to traffic are consequence of fuel combustion, vehicular component wear, road degradation and roadway maintenance. The traffic-related PM include in their compositions metallic elements with anthropogenic origin such as V, Cr, Fe, Ni, Cu, Zn and Pb (Sansalone and Buchberger [20]), and also elements resulting from crust and road abrasion such as Mg, Al, Si, Ca, K and Ba Viana *et al* [21]. The following 20 elements were determined using the PIXE technique to characterize PM_{10} and $PM_{2.5}$ sampled at the two traffic and two background sites: magnesium (Mg), aluminum (Al), silicon (Si), phosphorus (P), sulfur (S), chlorine (Cl), potassium (K), calcium (Ca), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), lead (Pb), bromine (Br), arsenic (As) and barium (Ba); however, as the number of PM samples with As, Ba and Br was not significant, these elements were not included in further evaluations. The mean concentrations of elements in PM_{10} and $PM_{2.5}$ and the SD at the traffic and the

background sites are presented in Table 2. The results demonstrated that: i) at both traffic sites the levels of Mg, Al, Si, P, S, Cl, K and Ca in both fractions were significantly higher than at background sites; ii) the highest levels of Ti, Cr, Mn, Fe, Ni, Cu and Zn in PM_{10} were recorded at Tr_1 being 3-44 times higher than at background sites; iii) the highest levels of Cr, Mn, Fe, Ni, Cu and Zn in $PM_{2.5}$ were observed at Tr_1 being 3-27 times higher than at the background sites; iv) the highest levels of Pb in PM_{10} were observed at Tr_1, being 6-9 times higher than at Bc_1; v) the highest levels of Pb in $PM_{2.5}$ were recorded at Tr_1, being at traffic sites 3-4 times higher than at Bc_1; vi) the levels of V in PM_{10} at traffic sites were 4 times higher with respect to the background sites; and vii) the levels of V in $PM_{2.5}$ at sites Tr_1 and Tr_2 were, respectively, 5 and 10 times higher than at the background sites. As expected, the obtained results showed that at sites influenced by traffic particle metal contents were significantly higher than at the backgrounds sites. Thus, traffic emissions influenced the compositions of both PM_{10} and $PM_{2.5}$, increasing greatly their levels of metals.

The concentrations of all elements in $PM_{2.5}$ versus PM_{10} were evaluated. For the traffic sites, around 80-90% of S, Mn, Zn and Pb present in PM_{10} were detected in $PM_{2.5}$. This percentage was lower for P, K and Cr (60-80%) and even lower (below 50%) for Mg, Al, Si, Ca, Ti, Fe, and Cu. In general, at both traffic sites, the elements originated mostly from anthropogenic activities were predominantly present in the fine fraction (S, Mn, Zn, Pb, P, K and Cr) while the elements mostly originated from crust (Mg, Al, Si and Ca) mainly occurred in the coarse particles.

At both background sites, more than 90% of Ti and S present in PM_{10} were found in $PM_{2.5}$; this percentage was lower for Mn (63%) and even lower for P (below 50%); however, more than those no other similarities between both background sites were observed. At site Bc_1 more than 90% of Cr, Cu, Zn and Pb present in PM_{10} belonged to $PM_{2.5}$. This percentage decreased for Mg, Al, Si and Ca (60-80%) and dropped below 50% for V. At site Bc_2 more than 90% of Mg, Al, Si and Fe present in PM_{10} belonged to $PM_{2.5}$. This percentage was lower for V, Cu and Zn (60-80%) and even lower (below 50%) for P, K, Ca, Cr and Cl. At site Bc_2, chlorine was mainly present in coarse particles (42% in $PM_{2.5}$), which was on the contrary to Bc_1 where 70% of Cl present in PM_{10} was detected in fine fraction. As it was already referred, Bc_2 was situated close to the seacoast. As sea salt sprays are mostly composed by coarse particles, the presence of Cl mainly in PM_{10} at Bc_2 can be attributed to marine influence, confirming the previously referred conclusion obtained through the analysis of $PM_{2.5}/PM_{10}$ ratios at the two background sites. Concluding, sea salt sprays influence concentrations and compositions of atmospheric background particles as well as the distribution of Cl between PM_{10} and $PM_{2.5}$.

4 Conclusions

Traffic emissions increased about 7-9 times PM_{10} concentrations and about 6-7 times $PM_{2.5}$ concentrations; sites influenced by traffic showed to be influenced mainly by that source.

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Table 2: Mean concentrations of elements in PM_{10} and $PM_{2.5}$ at the four sites (ng m^{-3}).

	Tr_1				Tr_2				Bc_1				Bc_2			
	PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$		PM_{10}		$PM_{2.5}$	
	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD	mean	SD
Mg	111	54.3	45.2	40.7	127	83.6	43.5	29.0	24.3	13.3	22.3	9.59	30.4	21.6	17.3	7.95
Al	1350	941	493	405	1640	808	835	376	401	299	263	230	192	205	105	95.3
Si	2430	1600	886	657	2360	1170	1220	637	555	410	395	280	239	294	171	93.1
P	30.2	14.9	19.4	8.70	22.8	11.5	13.2	6.12	9.40	6.49	4.94	4.42	3.67	2.18	0.90	0.24
S	1270	416	1280	434	1010	490	866	357	790	331	847	307	563	566	648	517
Cl	631	405	432	417	957	969	253	230	49.6	19.4	29.1	6.58	567	512	73.4	95.8
K	834	461	632	374	625	246	432	211	166	97.5	147	65.8	70.2	48.3	40.4	36.3
Ca	889	555	275	195	623	336	296	139	89.6	79.7	51.0	41.3	74.9	63.7	28.5	25.4
Ti	50.8	27.4	19.7	12.6	43.5	19.1	25.9	15.1	13.1	9.53	9.88	5.50	8.60	7.41	5.64	5.51
V	14.7	11.0	5.18	3.10	15.5	8.95	9.76	8.42	3.79	3.18	1.27	0.39	1.13	0.46	0.56	0.21
Cr	8.69	3.81	4.55	2.59	6.08	3.41	3.05	2.23	7.64	9.04	1.49	0.39	2.79	0.53	0.72	0.59
Mn	13.4	5.83	11.4	10.2	7.97	3.95	6.63	3.86	3.93	1.92	2.59	2.14	4.38	1.02	1.58	1.34
Fe	1550	671	583	301	810	330	395	194	136	84.7	78.5	62.9	48.7	62.5	31.3	38.4
Ni	8.29	4.46	4.86	4.03	7.41	5.27	5.37	3.90	5.64	5.74	2.19	1.30	-	-	-	-
Cu	87.3	40.2	32.2	17.0	39.0	17.3	18.6	8.60	4.86	3.61	4.26	4.05	1.86	1.52	1.65	1.21
Zn	172	104	134	86.5	104	54.1	83.7	48.7	20.1	15.8	20.2	10.9	7.84	6.42	4.91	3.76
Pb	55.5	27.1	43.4	11.4	33.9	17.0	30.9	17.8	5.83	1.12	10.8	0.88	-	-	-	-

Results with 3 significant figures.

Background PM_{10} fraction was almost composed by fine particles; the fraction of fine particles was higher than usual, which means that to develop strategies to protect public health is fundamental.

At sites influenced by traffic emissions, particle metal contents were for PM_{10} 3-44 times higher and for $PM_{2.5}$ 3-27 times higher than at the backgrounds sites; traffic emissions increased greatly the levels of metals.

The sea salt spray plays an important role as particle source in coastal areas, influencing the concentrations and composition of PM, as well as the distribution of related elements between coarse and fine fractions; when influenced by sea salt PM_{10} increased by 46%, $PM_{2.5}/PM_{10}$ decreased by 26% and Cl in PM_{10} was 11 times higher.

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Section 2
Air pollution modelling

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Modelling of carbon monoxide dispersion along roads with the use of the finite element method

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Abstract

CFD models are used in air protection to simulate the spreading of gaseous pollutants. The CFD models allow us to obtain the necessary information on the liquid flow (velocity and pressure distribution fields), heat and mass transfer. This is achieved by numerically solving the differential equations which describe momentum transfer as well as energy and mass balances.

The proposed model was based on a three-dimensional calculation grid, which represented a fragment of the environment around a considered road segment. The calculation grid was built from regular rectangular eight-node elements and mapped a two-lane road.

In the grid model, cubicoids representing automobiles and trucks were placed in an air flow. The size and number of the cubicoids corresponded to the mean size of automobiles, trucks, the traffic intensity and mean velocity. For such a system, equations of air flow turbulence were solved. Next, taking into account the estimated pollutant emission and solving mass transport equation, carbon monoxide concentration profiles were calculated. The system of partial differential equations was solved using the finite element method. The software proposed by the authors was used. To verify the method, measurements were made at a selected street in Lodz, measuring the level of CO, recording wind velocity and direction, temperature, pressure and air humidity as well as the degree of clouding and additionally recording the number and the vehicle motion. Based on the film, one can determine the intensity of vehicle motion classified into trucks and automobiles and average traffic velocity. The data was used not only to obtain model parameters, but also allowed us to assess accuracy of the prediction.

Keywords: traffic emission, pollution modelling, CO dispersion, finite element method.

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1 Introduction

The contribution of road transport to global air pollution is very high, and in industrialised countries it is equal or even exceeds the pollution generated by industry. On a global scale, cars release nearly 300 million tonnes of toxic exhaust emissions annually. It is estimated that big urban agglomerations in Europe are inhabited by 70–80% of its population. Due to the size and character of vehicle exhaust emission, local conditions which hamper quick ventilation of streets and a continually growing number of vehicles, the percentage of people exposed to the harmful effect of toxic components of vehicle exhausts is still very high.

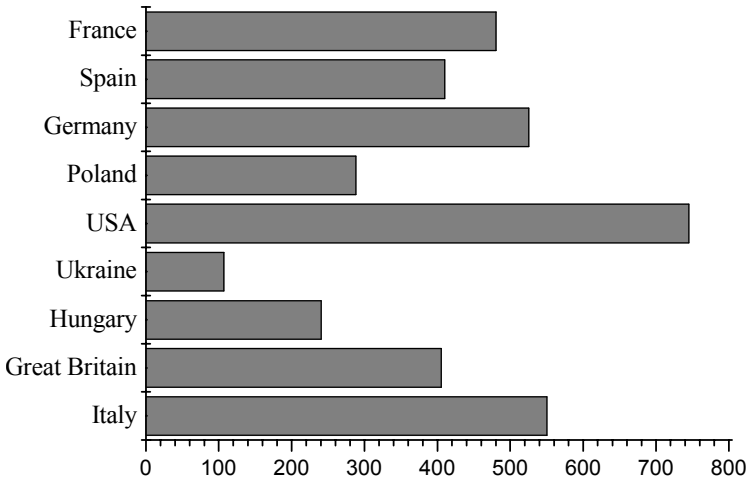

Figure 1: Number of cars per 1000 people in selected countries in 2000 (Statistical Yearbook, 2003).

According to the latest literature, street traffic can be treated as the main source of air pollution in big cities. In certain regions its contribution to the emission of carbon monoxide CO is estimated to be ca. 70% or even 90%, and the emission of nitric oxides NO_x amounts to 23%, while according to other authors this is 98% and 20%, respectively [1,2]. Carbon monoxide is also referred to as the biggest source of organic carbon emitted in the form of aerosols. According to researches carried out in Athens, street traffic is responsible for 8% of the pollution with sulphur dioxide SO_2, in 67% with nitric oxides NO_x, in 64% with hydrocarbons C_xH_y and in almost 100% with carbon monoxide CO [3].

Tools to estimate the effect of street traffic on air quality in urban agglomerations are based on various types of mathematical models. When assumed conditions are considered, it is possible to determine the behaviour of pollutants in a street canyon, open road, cross roads or even on a pavement.

Possible impacts of initial conditions, such as exhaust emissions and building layout, allow us to determine concentration fields of toxic substances in the air. Models that describe pollutant dispersion and transport in the air can be classified according to various criteria. One of them is space scale in which global, regional and local models can be distinguished. The next classification is made in reference to time, i.e. the time of averaging pollutant concentrations. American regulations give the period of 1, 3, 8 and 24 hours as the main reference times in short-term models, while in long-term models the averaging times range from 1 month to 1 year. The models of dispersion can also be divided into these which are used to calculate changes in the concentrations of toxic compounds during a set period of time in selected receptors and the models which calculate spatial concentration fields in a given time instant. An additional classification criterion is the degree of urbanisation. Here, we have urban and rural areas which differ in a roughness coefficient and meteorological exponent for subsequent classes of atmosphere equilibrium. Due to their complexity, the models can be divided into refined and screening ones. In the refined models numerous factors are taken into account, which enable much more precise calculation of concentrations. However, they require a large number of data which are not always easily available. The screening models are usually applied to roughly estimate pollution or to simulate changes in the trends of toxic compound concentrations [4]. Taking into account the mathematical approach, the models of pollutant dispersion can be divided into several main groups: box models, Gaussian models, receptor, Euler and stochastic models. The classification of models according to the above criteria is given by Vardoulakis et al. [5].

2 Description of the method

To simulate a phenomenon, process or object, its mathematical model should be known. It is usually composed of algebraic, ordinary differential, partial or integral equations. So, the simulation consists in solving a system of equations. In the case of vehicle traffic and gas pollutant dispersion, there is a turbulent fluid motion. Basic equations which describe such a flow are the Navier–Stokes equations. For an incompressible fluid the momentum conservation equation should be completed with a continuity equation.

$$\nabla \cdot \mathbf{u} = 0 \tag{1}$$

$$\nabla \cdot \left((\mu + \mu_t) \left(\nabla \mathbf{u} + (\nabla \mathbf{u})^{\mathrm{T}} \right) \right) - \nabla p - \rho \mathbf{g} = 0 \tag{2}$$

The turbulent viscosity coefficient in the Navier–Stokes equation is calculated from the Prandtl-Kolmogorov relation which refers to kinetic energy of dissipation K and the length of mixing path l_μ.

$$\nabla \cdot \left(\left(\mu + \frac{\mu_t}{\sigma_K} \right) \nabla K \right) + \mu_t \gamma^2 - \rho C_D \frac{K^{3/.2}}{l_\mu} = 0 \tag{3}$$

$$\mu_t = \rho C_\mu K^{1/2} l_\mu \tag{4}$$

where

$$l_\mu = \kappa \delta \tag{5}$$

δ – distance from the nearest wall, γ – local shearing rate, κ – von Karman constant, σ_K – turbulent Prandtl number, C_D, C_μ – empirical coefficients.

The system of equations was completed with a pollutant transport equation, in which the release rate of a pollutant, i.e. carbon monoxide emission source, was considered.

$$\frac{Dc}{Dt} = \nabla \cdot \left((D + D_t) \nabla c \right) + Q \tag{6}$$

$$c = f\left(x(t), y(t), z(t), t\right) \tag{7}$$

The turbulent diffusion coefficient was determined from the equation:

$$D_t = \frac{\mu_t}{Sc} \tag{8}$$

where:

μ_t turbulent viscosity
Sc Schmidt number

The proposed system of equations with boundary conditions was solved using the finite element method [6]. A road segment 80 m long is analysed in the model. The analysed segment is a two-lane road 7.5 m wide with 20 m shoulder on each side. The analysed height above the road level was 15 m. Vehicles in the calculations were represented by cubicoids of dimensions equal to average dimensions of passenger vehicles and lorries. It was also assumed that pollutant dispersion was an isothermal process. The emission and dispersion of carbon monoxide were considered in the calculations. Carbon monoxide emission was estimated according to Copert 3 algorithm [7]. Statistical data concerning the number of cars, engine size and CO emission, with reference to various aspects of operation of combustion and diesel engines, was included in the calculations.

Calculations were started with the determination of a velocity profile. It was assumed that the CO concentration profile was a result of two overlapping

effects: motor traffic and turbulence caused by the traffic as well as air flow resulting from meteorological conditions (wind direction and velocity). These effects were included in two subsequent procedures of velocity field calculation. At the first stage, cars were motionless while the environment was moving at a velocity resulting from mean vehicle velocity. An initial condition at this stage of calculations was a constant initial velocity of the moving environment. As a result of an iteration, a profile of air flow along the road was formed. The profile was recorded by a computer. Next, a velocity profile resulting from air flow was calculated. It was calculated irrespective of the previous profile. At this stage the air flow was also assumed to be constant. Using iteration, a proper velocity profile was obtained both in the vicinity and on the road.

In the proposed model of pollutant dispersion, the calculations were divided into two stages. The principle of superposition was also used. The first stage covers exhaust emission and dispersion resulting from motor traffic (velocity profiles from the first stage of the simulation). At the second stage there is a further dispersion due to air flow resulting from atmospheric conditions. During simulation, the above discussed stages followed each other until reaching a steady state. For exhaust emissions, the initial concentration on the road was zero. Next, as a result of exhaust emission and dispersion a concentration distribution was obtained. The concentration profile was also modified in subsequent iterations until reaching the steady state.

3 Measuring methods

Measurements were taken near a two-lane road with heavy traffic. The measuring set-up was situated on a straight road segment within Lodz boundaries. On the whole, a series of ca. 177 measurements were taken in the spring and autumn season. The measured substance was carbon monoxide because of its amount formed during liquid fuel combustion and especially harmful impact on the health of people in general and car drivers in particular.

The concentration of carbon monoxide was measured by a CO12M analyser (Environment S.A.) used for analyses in continuous or batch systems. The device is especially useful at low pollutant concentrations in the ambient air in atmospheric conditions and is characterised by a detection limit of 0.05 ppm. Its operation is based on detecting the rate of absorption of infrared radiation. To measure temperature, humidity and wind velocity, an ALMEMO 2290-3 device (Ahlborn, Germany) was applied. Additionally, the traffic was filmed by a JVC camera. Based on the records, the number, types and average driving speed of the vehicles were determined. The recorded data is given in Table 1.

4 Results and discussion

Simulation, made by means of the model described above, consisted of solving the proposed system of equations in all nodes of the assumed calculation domain and determination of the concentration fields of the considered pollutant in time

and space. Results obtained in this way allowed us to obtain concentrations in arbitrary cross sections of the calculation grid. The calculations were made for all input data taken from real measurements and they were compared with the measured carbon monoxide concentrations. Figures 2 and 3 show the effect of wind velocity and traffic intensity on the concentration profile, respectively.

Based on the data obtained, the CO concentration on the road edge was recorded in the locations in which the measurements were actually taken. A comparison of experimental and calculated data is given in Table 2.

The correlation coefficient was compared with the values of R found in literature for other grid models (Table 3).

Table 1: Measurements taken on the road – the type and range of values.

Measured value		Range	
1	Traffic density of passenger cars	car/s	0.37 – 0.70
2	Traffic density of lorries	lorry/s	0.008 – .038
3	Level on which CO concentration was measured	m	0 – 1.5
4	Wind direction	o	0 – 360
5	Wind power	m/s	0 – 3.4
6	Air temperature	°C	2 – 27.9
7	Moisture content	%	33.2 – 94.4
8	Total cloud amount	-	1/8 – 8/8

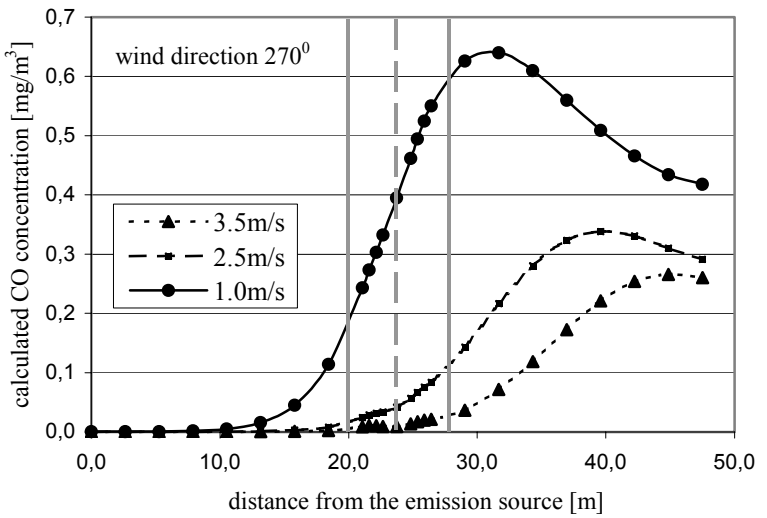

Figure 2: A comparison of concentration profiles for different wind velocities.

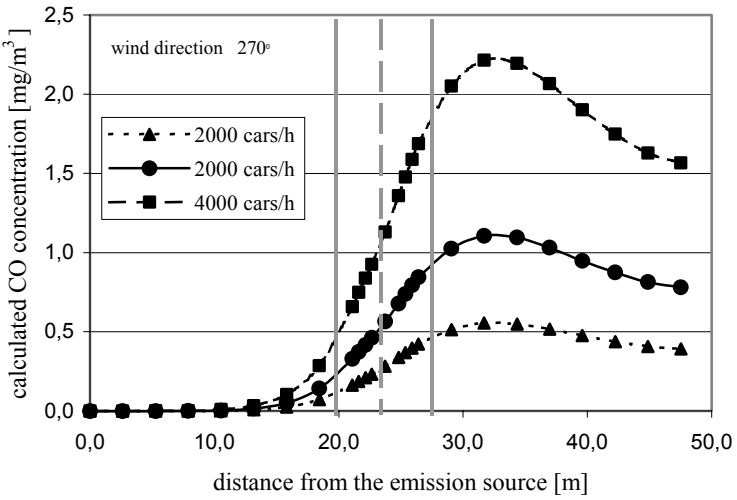

Figure 3: A comparison of concentration profiles for different traffic intensities on the road.

Table 2: Statistical evaluation of the grid model.

	Wind direction			
	180°	220° – 230°	270°	220° – 230°
Correlation coefficient, R	0.80	0.83	0.77	0.83
Root mean square error,δ	0.31	0.39	0.30	0.40

Table 3: Comparison of the proposed model and other grid models.

Model	R	Literature source
Our model	0.81	-
Miskam	0.69	Lohmeyer et al., 2002 [8]
OSPM	0.80	Berkowicz et al., 2002 [9]

5 Conclusions

1. The grid model used in the recording of specific situations on the road, despite the application of relevant equations which describe fluid flow and exhaust dispersion, requires far reaching simplifications resulting from complexity of the studied issue.

2. The main advantage of the proposed model is that carbon monoxide concentration can be determined in an arbitrary point of the considered calculation domain.
3. Accuracy of the calculated values is a result of the assumed simplifications and estimated CO emission.

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Air velocity and pollutant profiles in Krakow

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Abstract

This paper presents a numerical grid model based on the finite element method, which enables a computer simulation of air mass flow and pollutant propagation over Krakow. To construct a calculation domain the information from a digital map was used, which allowed us to include an active surface layout into the model.

Methods for implementation of velocity fields from a mesoscale meteorological pre-processor as a boundary condition for the model in the city scale were developed. Air velocity profiles over Krakow, calculated from the MM5 meteorological model data are presented. Additionally, the evolution of a concentration field for a hypothetical tracer release in the city was simulated.
Keywords: air flow field, modelling of pollutants propagation, meso- and macroscale model.

1 Introduction

A key problem in the modelling of pollutant dispersion over strongly urbanised areas is to reflect the effect of local factors on the formation of a velocity profile. A wind field over the city is characterised by a significant spatial differentiation, which in turn determines the processes of transport and dispersion in lower layers of the atmosphere. As a result of the impact of obstacles in the city, flow turbulence increases, the so-called tunnel winds resulting from deep street canyons, flow swirls, and even streams in the direction opposite to average wind are formed [1,2]. It is also important to take into account velocity profiles varying in time, particularly when meteorological conditions over the considered area are changing. Data from the mesoscale

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meteorological model MM5 (*Penn State University/National Centre for Atmospheric Research's Mesoscale Model*), was used in the calculations for Krakow.

The idea of the proposed research is to develop a computer model of air pollutant dispersion in lower layers of the atmosphere over Krakow using the finite element method FEM and a general Euler–Lagrange approach [3,4]. The model will reflect topographic features and buildings on a given area, as well as arterial roads. These elements have a fundamental effect on the dispersion of air pollutants on an urbanised area. The similar approach was presented in our previous paper which took Lodz (city in Poland) as an example [5].

The proposed method is a compromise between too general mesoscale models and microscale models, whose application in the described task would require a significant processor capacity.

2 Construction of a calculation domain

The proposed method allows us to include in the calculation domain geometry the elements typical of strongly urbanised areas, i.e. building structure and arterial roads, as well as the natural surface features. For this purpose a digital map was used. The map contained coordinates which describe topography of Krakow and also information on the character of built-up areas and location of main roads. Basing on the digital map sub-regions with relatively uniform buildings in view of their height were selected. Additionally, on the urban built-up areas the network of arterial roads constituting ventilation ducts for the city was distinguished. The roads were classified according to their type and width, proportionally to the ventilating functions. A 3D calculation domain grid, containing the above elements, was constructed. In numerical calculations our own software was used, which allowed us to consider many details that made the model closer to reality and which were not available in a typical commercial software.

At the first stage of the calculation process, the Navier–Stokes and mass conservation equations were integrated, which enabled determination of velocity profiles of the flowing air masses [6]. At the second stage, the equation of pollutant transport in the atmosphere was solved basing on the previously formed velocity profile. As a result, a continuous concentration profile and its evolution in time were obtained.

To define boundary conditions, the authors used meteorological data concerning the direction and velocity profile of air flowing over the studied area, taken from MM5 the mesoscale prediction model.

To determine precisely the construction of a calculation domain, a digital map describing topographic features of Krakow and its neighbourhood, i.e. the area 36.1 × 23.6 km (Figure 1) was used.

Additionally, basing on an electronic map of the road system in the city, a representation of arterial roads which can be ventilating ducts for Krakow was included in the model grid (Figure 2). The 3D calculation domain contains a space from the ground or building surface (depending on the character of surface cover) to the height 700 m above sea level.

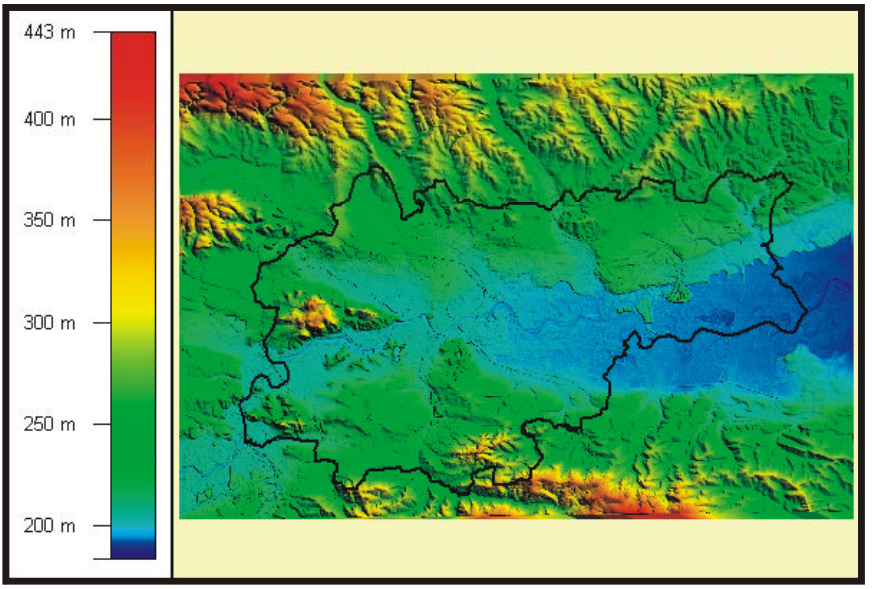

Figure 1: Topographic features of Krakow and neighbourhood.

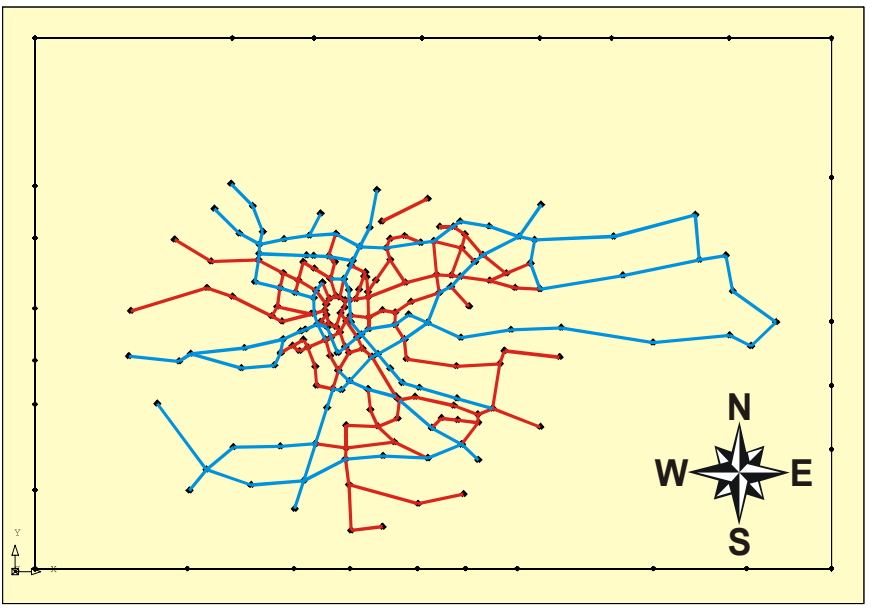

Figure 2: Arterial roads in Krakow included in the model.

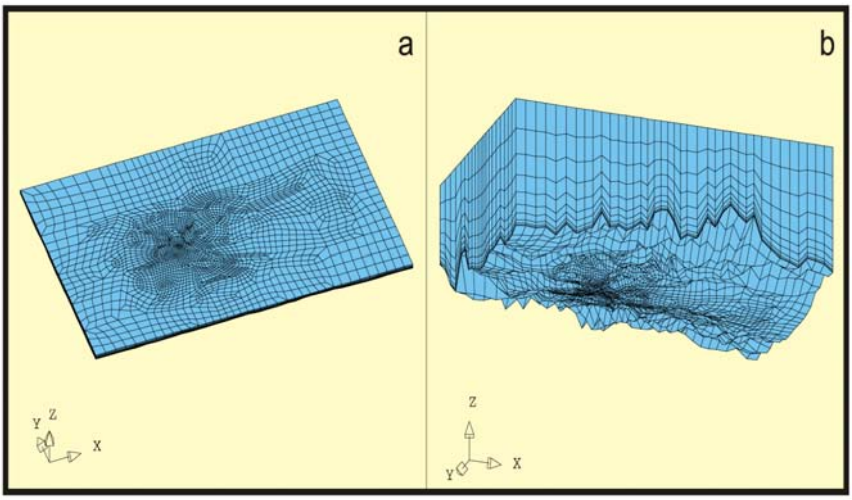

Figure 3: A 3D grid of the calculation domain a) real dimensions, b) vertical dimension extended for better visualisation.

Basing on the digital map, each point of the calculation grid was referred to a real position above sea level. The grid with a variable calculation mesh was so constructed as the higher resolution encompassed the town area with dense down-town buildings and was decreasing while receding from the city centre. The grid of the model was concentrated in the near-surface zone, where the highest differentiation of the velocity profile was expected.

An irregular shape of the elements of the calculation grid was a result of the representation of arterial roads and the Vistula river in the model (Figure 3). These obstacles were located on the basis of the electronic map which contained detailed information on the structure of the road system in Krakow.

3 A mathematical description of air velocity profile modelling

At the first stage of the calculation process velocity profiles of air flowing over the city were determined. The continuity equation with liquid incompressibility assumption and Navier–Stokes equation for three directions were used to describe air flow over Krakow.

$$\nabla \cdot \mathrm{u} = 0 \tag{1}$$

$$\nabla \cdot \left(\left(\mu + \mu_t \right) \left(\nabla \mathrm{u} + \left(\nabla \mathrm{u} \right)^{\mathrm{T}} \right) \right) - \nabla \mathrm{p} - \rho \mathrm{g} = 0 \tag{2}$$

The so-called one-equation turbulence model (K-model) was included to liquid motion (eqn. (3)). This allowed us to take into account the turbulent character of air flow. Turbulent viscosity μ_t expressed by the kinetic energy of fluctuation K was introduced eqn. (4). The K-model requires relatively small

calculation outlays, and the obtained results are comparable with more complicated models of turbulence, as e.g. k-ε [2].

$$\nabla \cdot \left(\left(\mu + \frac{\mu_t}{\sigma_K} \right) \nabla K \right) + \mu_t \gamma^2 - \rho C_D \frac{K^{3/.2}}{l_\mu} = 0 \tag{3}$$

$$\mu_t = \rho C_\mu K^{1/2} l_\mu \tag{4}$$

where

$$l_\mu = \kappa \delta \tag{5}$$

δ – distance from the nearest wall, γ – local shearing rate, κ – von Karman constant, σ_K – turbulent Prandtl number, C_D, C_μ – empirical coefficients.

On the surface limiting the calculation domain from the bottom, the following boundary conditions were applied:

$u = 0$ – zero components of velocity vectors u in all three directions,

$K = 0$ –kinetic energy of fluctuation *K* equal to zero.

On the remaining surfaces, where u and/or K were not defined, zero components of momentum flux and/or turbulent energy in normal direction were imposed:

$$\left(-p \cdot I + (\mu + \mu_t)\left(\nabla u + (\nabla u)^T\right)\right) \cdot n = 0 \tag{6}$$

$$\frac{dK}{dn} = 0 \tag{7}$$

For a simplified representation of the most important transport roads, on the lines which corresponded to arterial roads, the condition of zero velocity components in horizontal directions was assumed. The calculated values were corrected by drag coefficients which were selected taking into account the widths of arterial roads, and also their importance for city ventilation. In the case of Krakow two categories of ventilating ducts were distinguished (Figure 2).

3.1 Examples of simulation results

A method was developed to include time-variable wind field in the presented model by implementing boundary conditions in the form of velocity profiles from the meteorological model of a lower resolution.

Average, hourly velocity profiles of 28 Feb. 2006, generated by MM5 meteorological pre-processor, interpolated to the height 700 m above sea level were used in the presented results of the simulation. Since the data from the MM5 model referred to the grid with mesh size 6 km × 6 km, it was necessary to

apply the interpolation to model resolution in the city scale, i.e. transfer to the macroscale model. The finite element method was used in the developed interpolation procedure.

As a result of numerical calculations (the first stage) the air velocity profiles over Krakow in the entire 3D calculation domain shown in Figure 4 were obtained.

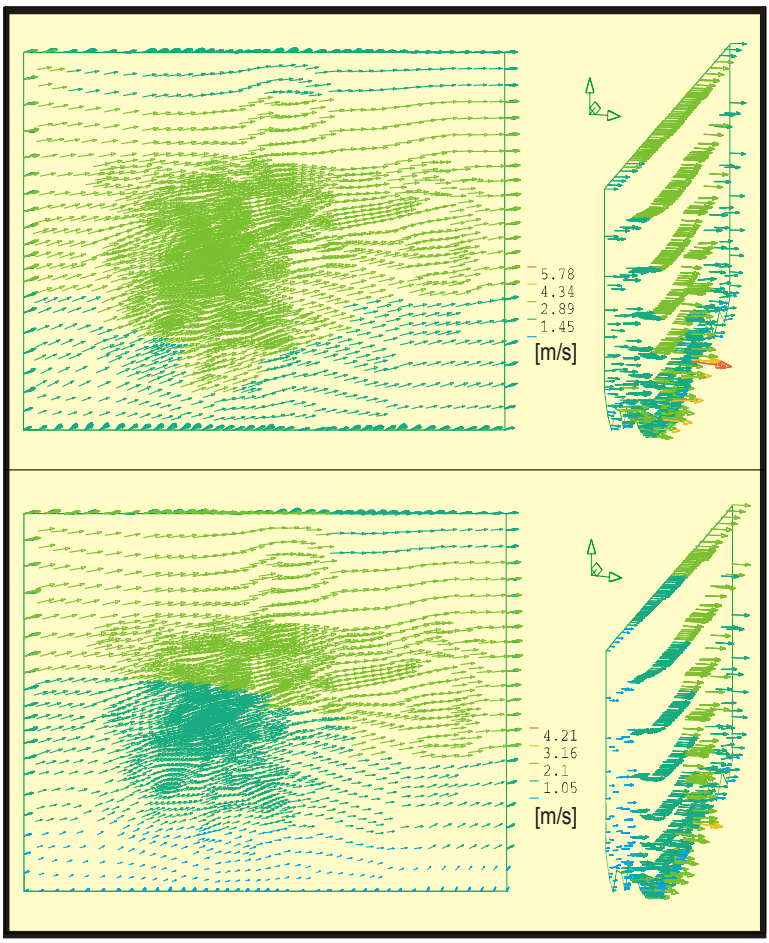

Figure 4: Velocity profiles for boundary conditions obtained from MM5 on 28 Feb. 2006 a) 12:00 GMT + 1H b) 12:00 GMT + 5H.

4 A mathematical description of pollutant dispersion models

At the second stage, using the previously determined velocity profiles, the advection-diffusion pollutant transport equation was solved. In numerical calculations the original Lagrange algorithm was used (eqn. (9)).

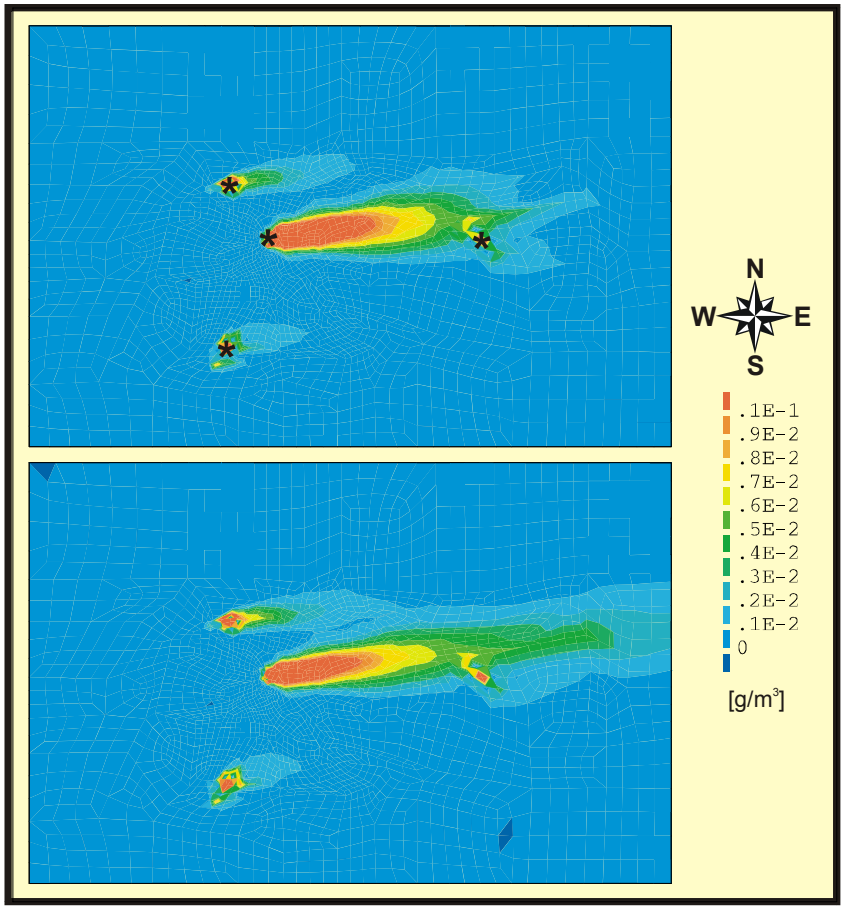

Figure 5: Concentration profiles of pollutants emitted on building level in pointsdenoted by symbol *, a) after 1 h since the incident b) after 5 h since the incident.

$$\frac{Dc}{Dt} = \nabla \cdot \left(\left(D + D_t \right) \nabla c \right) + Q \tag{8}$$

$$c = f\left(x(t), y(t), z(t), t \right) \tag{9}$$

4.1 Examples of simulation results

The wind velocity profiles allowed us to simulate the dispersion of a hazardous substance (tracer), released for instance as a result of industrial accident in the city (0.2 kg/s at each point). In modelling of this phenomenon variable meteorological conditions referring to wind velocity and direction were taken into account. The examples of calculations are illustrated in Figure 5.

5 Concluding remarks

A three-dimensional numerical macromodel is proposed. The model is a compromise between mesoscale models, in which it is impossible to include the effect of local factors on velocity profile formation and pollutant transport processes. Macroscale models for the whole city do not require a significant processor capacity.

A method referring to time-variability of the velocity profile in the model in the city scale, using the so-called nesting in the meteorological model of lower resolution (MM5), was proposed.

The procedure enables a simulation of hypothetical emissions of hazardous substances which take place in different points in the city, for different meteorological conditions referring to the velocity and direction of flow of air over the tested area.

This will allow us to formulate probable scenarios of the evolution of hazard propagation. Parts of Krakow particularly exposed to elevated levels of deposition will be indicated, which can be useful in planning rescue operations to minimise effects of incidents.

Reliability of predictions of the proposed macromodel depends to a large extent on the quality of data generated by the meteorological preprocessor.

6 Nomenclature

K	–	the kinetic energy of fluctuation [m^2/s^2]
ρ	–	liquid density [kg/m^3]
μ_t	–	turbulent liquid viscosity [Pa s]
μ	–	liquid viscosity [Pa s]
δ	–	distance from the nearest wall [m]
u	–	velocity [m/s]
Q	–	pollutant release rate [kg/s]
p	–	pressure [Pa]
k	–	von Karman constant
g	–	acceleration [m/s^2]
D_t	–	atmospheric turbulent diffusion coefficient [m^2/s]
D	–	molecular diffusion coefficient [m^2/s]
C_D, C_{m-}		empirical coefficients
σ_K	–	turbulent Prandtl number [-]
γ	–	local shearing rate [1/s]

Acknowledgements

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Optimizing the prediction models of the air quality state in cities

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Abstract

The aim of research was to optimize the neural networks models for predicting the classes of air quality state. This model was constructed and tested on the basis of the data gathered in Lodz, a city localized in the middle of Poland. Models were tested in relation to mean daily dust concentration (PM_{10}) as well as maximal daily values. In each case, 5 air quality classes were distinguished. Air quality in each day was classified with respect to the meteorological conditions. Two models were built: two artificial neural networks (ANNs) were used, namely the MLP and the RBF. Optimization relied on determining the value of the following optimal value of the following ratio of the training set to the testing set, neuron number, number of input vectors after the PCA dimension reduction procedure.

Results of the modelling are satisfactory. The error for predicting the air quality classes was generally smaller than 13%. In relation to predicting air quality classes, mean daily PM_{10} concentrations, better results were obtained with the RBF model containing 5 neurons. The RBF model for maximal daily PM_{10} concentrations generates a classification error of about 10,7%, and MLP model generates an error of 14,9%.
Keywords: artificial neural network, classification, PM_{10},

1 Introduction

A feature of the climate in large cities is the unsatisfactory condition of the atmospheric air due to human activity. Unneeded interactions are due to the functioning of the developed road transport, many branches of industry located in a small area as well as realization of the life and economic needs such as

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compartments heating [1]. As an effect the danger of high concentration of air pollution may arise, which may have negative influence on the health and even the life of many citizens. In managing the air quality for the large cities the diagnostic and prognostic models play a vital role. The development of such tools is a complicated task. The process of forming the deposition fields are dependent on many various factors with strong variability of parameters. Moreover, difficulties result from strong dynamics of atmosphere as well as nonlinearities and incomplete recognition of atmospheric processes and imperfections in the monitoring network [2]. Taking all elements and conditions into account is impossible. In practice, the range of available data is limited, therefore farfetched simplifications are applied in models, especially numerical models.

Artificial Neural Networks (ANNs) are a proven tool for deposition concentration fields description. Due to their ability to generalize dependencies and reduce impact of secondary factors ANNs allow one to use incomplete measurement data burden with errors. ANN are especially useful in forecasting pollution level in cities, where complexity of problem preclude different methods of modeling. Many works with similar approach can be stated [3–7].

The atmosphere monitoring system in Poland was greatly improved. The higher quality and extended range of atmosphere monitoring allows a more precise determination of air quality characteristics and effect-reason analysis. Possibility of determination and analysis the daily concentration charts is very valuable. In previous years this was not possible due to the generation of less reliable results and the only results available were 24-hour mean air pollution concentrations. Recognition of the scale, specific and conditions of the 24-hours variability in the concentrations significantly improves basis of the air protection management, especially predicting the mean and maximal concentrations.

2 Territory and scope of research

The testing ground for our research was the city of Lodz (population: 800 000) located in the center of Poland. In the present paper the results of prediction concern the dust pollution (PM_{10}) in the densely build city center, where state of air quality is determined with the pollution emission originated with low emitters (individual house furnaces). Results obtained in the period starting from 1 January 2004 and ending 28 February 2006 at an automatic monitoring station located in the city center were used.

A typical feature of the daily run of the dust concentration PM_{10} during the winter season is presence of two distinct maxima: lower from 9^{00}-10^{00} and higher from 17^{00}- 19^{00} (Fig. 1). Daily minimal dust concentration occurs from 04^{00}-06^{00}. At the station located amongst housing estates the amplitude of daily concentrations is only 18 $\mu g/m^3$, due to small values of daily maxima. At the stations located in the city center a decrease in the concentration (by the 20 $\mu g/m^3$ compared to the afternoon maxima) at midday can be clearly seen. The period of the relatively high PM_{10} concentrations lasts – in winter season – more than 12 hours (from 08^{00} to 21^{00}).

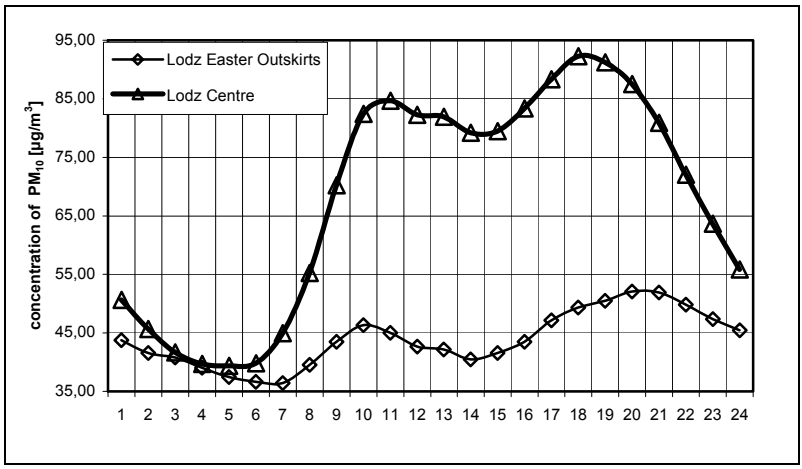

Figure 1: Daily changes of mean values of PM_{10} dust concentration in winter seasons 2004-2006 (I, II, XII) for monitoring stations localized in Lodz.

PM_{10} concentration during the summer season is significantly lower than during the winter. Even in the city center the mean daily maximal values are twice lower than the winter maxima. Main summer maximum occurs only at 20^{00}-22^{00} hours, and secondary maximum at 06^{00}-08^{00} hours. As a consequence the near-noon period of decreased concentrations during summer lasts a few hours longer than during winter. In this period PM_{10} concentrations in cities can be as high as 30-35 $\mu g/m^3$. Daily minima on all city stations are as low as 25 $\mu g/m^3$. These minima are registered during night hours (02^{00}-04^{00}).

3 Model optimization procedure

To forecast air quality the determination of the precise concentration value is not always needed. To warn citizens on high air pollution concentration hazards of ranges (classes) of forecasted values of concentrations were determined. The aim of our research was to optimize the neural networks models for the predicting classes of air quality state.

Measured data of the dust pollution concentration were grouped into 5 class ranges depending on the concentration value. The class width was declared according the effective standards of the air quality (and multiplication factor of these standards, e.g. 50%, 100%, 150% of the standard values). The size of the created range of classes and number of cases for each class are shown in Tables 1 and 2. A similar approach was presented by Perez and Reyes [8].

Within the frames of present work two series of air quality classification were made. The first classification comprises distributions based on maximal daily value (Table 1) of the PM_{10} concentration between hours 08^{00}-20^{00}. The second classification was based on mean daily values (Table 2) of the PM_{10}.

concentration. Additionally, for each classification meteorological conditions for given measurement day were assigned.

To classify air quality in the aspect of state of dust pollution two types of artificial neural networks were used. First was artificial neural network of multi-layer perceptron (MLP) type with one layer of hidden neurons. In the second state of simulation neural networks of the Radial Basic Function (RBF) type was used. Additionally, a Principal Component Analyses (PCA) procedure was used to decrease dimension of input vectors (number of meteorological data).

PCA methods allow us to increase number of neurons in the hidden layer keeping constant total number of weights in neural networks. To have comparable results for each version the number of weights in neural networks should be similar.

Table 1: Characteristics of input data used in air quality classification in aspect of maximal PM_{10} concentration during day.

Parameter	Classes of PM_{10} concentration[$\mu g/m^3$]				
	I	II	III	IV	V
Range of classes [$\mu g/m^3$]	1-49	50-99	100-149	150-199	>200
Number of cases	25	89	68	33	25
Mean value of maximal concentration during day	40,9	76	123,6	167,9	284,2
Mean daily sum of rainfall [mm]	1,19	0,75	0,47	0,16	0,32
Mean daily sum of radiation [W/m^2]	366,3	503,1	775,9	819,9	1257
Mean daily wind velocity [m/s]	4,6	3,6	3,1	2,7	2,36
Mean daily vertical velocity [m/s]	-0,01	-0,07	-0,13	-0,09	-0,12
Mean maximal daily temperature [°C]	1,9	0,3	-0,6	-2,5	-4,07
Mean daily minimal temperature [°C]	-1,3	-3,3	-4,3	-6,8	-10,8
Mean daily atmospheric pressure [hPa]	985	989	990	990	994

Table 2: Characteristics of input data used in air quality classification in aspect of mean PM_{10} concentration during day.

Parameter	Classes of PM_{10} concentration [$\mu g/m^3$]				
	I	II	III	IV	V
Range of classes [$\mu g/m^3$]	1-25	25,01-50	50,01-75	75,01-100	>100
Number of cases	16	82	59	52	31
Mean value of maximal concentration during day	20,8	38,6	61,5	85,6	153
Mean daily sum of rainfall [mm]	1,36	0,86	0,45	0,38	0,13
Mean daily sum of radiation [W/m^2]	296,1	509,0	633,2	864,8	1173,1
Mean daily wind velocity [m/s]	4,7	3,7	3,1	2,8	2,2
Mean daily vertical velocity [m/s]	0,01	-0,07	-0,09	-0,14	-0,16
Mean maximal daily temperature [°C]	1,8	1,0	-0,9	-1,8	-3,8
Mean daily minimal temperature [°C]	-1,2	-2,4	-4,5	-6,4	-9,8
Mean daily atmospheric pressure [hPa]	984	989	990	990	992

Neuron model optimization relies on determination:

- ratio of the size of the training file against test file for the model (4 versions: test file was 17%, 20%, 25% and 33% of the all data file);
- number of neurons hidden in the MLP model (3 versions: 3, 5 or 7 neurons);
- number of input vectors characterizing meteorological conditions in the form of real meteorological conditions or orthogonal components obtained thanks to PCA;
- information on air quality in previous day.

Table 3: Characteristics of input vectors in the MLP calculation of the air quality.

Calculation case	ANN type	Information on meteorological conditions	Information on state of air pollution	Number of hidden neurons	Number of weights
1.	MLP	7 meteorological vectors	Max value of daily and previous day concentration	5	51
1a.		5 orthogonal components		6	49
1b.		3 orthogonal components		8	49
2.	MLP	7 meteorological vectors	Max value of daily concentration; max and mean values for the previous day	5	56
2a.		5 orthogonal components		6	55
2b		3 orthogonal components		8	57
3.	MLP	7 meteorological vectors	Mean value of daily and previous day concentration	5	51
3a.		5 orthogonal components		6	49
3b.		3 orthogonal components		8	49
4.	MLP	7 meteorological vectors	Mean value of daily concentration; max and mean value for previous day	5	56
4a.		5 orthogonal components		6	55
4b		3 orthogonal components		8	57

On the first stage of optimization the size of test file and number of neurons/centers in the network was determined. Calculations shown that error of forecasting the air quality class is the smallest if:

- test file size is 20% of available data file size;
- in the network there are 5 hidden neurons in the MLP model and 5 centers in the RBF model.

On the second stage we concentrated on network input vector structure optimization in the aspect of meteorological data and data on previous day PM_{10} concentration (Tables 3 and 4).

Table 4: Characteristics of input vectors in the calculation of the air quality classification with the ANN of the RBF type.

5.	RBF	7 meteorological vectors	Max value of daily and previous day concentration	5	50
5a.		5 orthogonal components		6	48
5b.		3 orthogonal components		8	48
6..	RBF	7 meteorological vectors	Max value of daily concentration; max and mean values for the previous day	5	55
6a.		5 orthogonal components		6	54
6b		3 orthogonal components		8	56
7.	RBF	7 meteorological vectors	Mean value of daily and previous day concentration	5	50
7a.		5 orthogonal components		6	48
7b.		3 orthogonal components		8	48
8.	RBF	7 meteorological vectors	Mean value of daily concentration; max and mean value for previous day	5	55
8a.		5 orthogonal components		6	54
8b		3 orthogonal components		8	56

4 The results of classification

All calculations were made for two types of neural networks (MLP and RBF). Air class forecasting in the aspect of the mean daily and maximum daily PM_{10} concentration has been done separately. In some cases model was tested with the PCA method with changes in the input vectors dimensions.

The results of air quality class forecasting were determined in a three-stage arrangement:

Stage I– good results: difference between calculated and real class is equal to 0 (full conformity of the forecast with reality),

Stage II– acceptable results (correct): difference between calculated and real class is +/-1 (forecast differs from reality by one concentration class),

Stage III– no acceptable results (erroneous): difference between calculated and real class is greater than +1 and smaller than –1 (forecast differs from reality by more than one concentration class).

All calculations have been made for the training and test series. In training series the rate of good results obtained with the MLP neural network was from 66,7% (for 4th case) to 49,5% (for 2b case), and for RBF neural network such rate was from 56,8% (for 8 case) to 46,9% (for 6a case). The rate of erroneous results in the training series was:

- for the MLP network minimal rate of erroneous results was 0 (for calculation case 3) and maximal rate was 6,8% (for case 1a),
- for the RBF network minimal rate of erroneous results was 1 (for calculation cases 7 and 8) and maximal rate was 7,8% (for case 6a).

Results obtained in test series were discussed in detail. Results for all cases are shown in Tables 5-8.

In the first series (calculation cases 1, 3, 5, 8) of calculation input vector consisted of information on the following:

- on air pollution state (1 vector) in the previous day; It was maximal PM_{10} concentration value during the day or mean daily PM_{10} concentration value, depending on the case,
- on meteorological condition in the given day (7 components of the input vector).

In this series the best results were obtained using RBF neural network (calculation case 7). In this case the highest rate of good results (61,7%) and 2% of erroneous results was obtained for the test series (Table 8).

Table 5: Results of the forecasting the air quality class for the daily maximal PM_{10} concentration in the Lodz's city center during winter seasons 2004-2006 using ANN of MLP type.

Calculation case	Rate (%) of results in test series		
	good	acceptable	erroneous
1.	46,8	42,6	10,6
1a.	40,5	46,8	12,7
1b.	34,1	57,4	8,5
2.	38,3	55,3	6,4
2a.	38,3	44,7	17,0
2b.	51,1	38,3	10,6

In the second series (calculation cases 2, 4, 6, 8) the information on PM_{10} pollution state was extended in such a way that input vector contained maximal and mean daily concentration values for the previous day. The meteorological vector remained unchanged.

In this series the best results were obtained using ANN of RBF type (calculation case 8). For the test series the high rate of good results (57,4) and zero rate of erroneous results was obtained (Table 8).

Table 6: Results of the forecasting the air quality class for the mean daily PM_{10} concentration in the Lodz's city center during winter seasons 2004-2006 using ANN of MLP type.

Calculation case	Rate (%) of results in test series		
	good	acceptable	erroneous
3.	59,6	38,3	2,1
3a.	44,7	46,8	8,5
3b.	31,9	57,4	10,7
4.	40,4	55,3	4,3
4a.	38,3	46,8	14,9
4b.	42,6	44,7	12,7

In the third series (calculation cases: 1a, 2a, 3a, 4a, 5a, 6a, 7a, 8a), the meteorological vector was modified. Vector, consisting of 7 values was

transformed to 5 orthogonal vectors. Results obtained in this series are not satisfactorily, because of the decrease in the rate of good results and significant increase in the rate of erroneous results.

Table 7: Results of the forecasting the air quality class for the maximal daily PM_{10} concentration in the Lodz's city center during winter seasons 2004-2006 using ANN of RBF type.

Calculation case	Rate (%) of results in test series		
	good	acceptable	erroneous
5.	48,9	46,8	4,3
5a.	40,4	48,9	10,7
5b.	51,1	42,6	6,3
6.	53,2	40,4	6,4
6a.	44,7	46,8	8,5
6b.	40,4	48,9	10,7

In the fourth series of calculations (calculation cases 1b, 2b, 3b, 4b, 5b, 6b, 7b, 8b) meteorological vector was transformed to three orthogonal vectors. Significantly better results compared to earlier calculation series were obtained only for cases 2b, 4b and 5b (Table 5-7). In each case the rate of good results was higher than 50 %. The rate of erroneous results was from 6% to 12 %.

Table 8: Results of the forecasting the air quality class for the mean daily PM_{10} concentration in the Lodz's city center during winter seasons 2004-2006 using ANN of RBF type.

Calculation case	Rate (%) of results in test series		
	good	acceptable	erroneous
7.	61,7	36,2	2,1
7a.	46,8	44,7	8,5
7b.	38,3	57,4	4,3
8.	57,4	42,6	0,0
8a.	44,7	51,1	4,2
8b.	44,7	46,8	8,5

5 Conclusions

The possibility of forecasting of the air quality classes in cities using neural network modeling was analyzed. Obtained results are satisfactory and thus confirming the usability of neural networks for solving such a class of problems. Taking into account all calculation cases (24) for both types of neural networks, mean error in forecasting the air quality class is 8%; greatest error is 17%, the smallest – 0%.

Simultaneously, the results of our work indicate the necessity of model optimization considering various conditions, especially in relation to number and type of input vectors. Comparing the optimization results of the air quality classification models for each calculation case, the following conclusions can be made.

- The greatest rate of good results was obtained in calculation case 7, when air quality class was forecasted in respect of mean daily PM_{10}, concentration, using RBF type network without implementing the PCA method considering mean daily PM_{10}, concentration for the previous day (Table 8),
- The lowest rate of erroneous results was obtained in calculation case 8, when air quality class was forecasted in respect of mean daily PM_{10} concentration using RBF network without implementing the PCA method considering mean daily PM_{10} concentration for previous day and maximal concentration value for previous day (Table 8),
- Using the same type of neural network better results were obtained for calculation cases using mean daily PM_{10} concentration.
- Only in three cases results were better with PCA method (calculation cases 2b, 4b i 5b; Tables 5-7),
- Using the same input vectors in the various neural networks slightly better results were obtained using RBF type network,
- Apart from network type and calculation case slightly better results of the air class forecasting were obtained in relation to the mean daily value of PM_{10} concentration; slightly worse results of air quality class forecasting for maximal daily PM_{10} concentration may result due to the small number of the highest concentration cases; it may be a barrier on the network training stage.

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Evaluation of industrial sources' contribution to PM10 concentrations over a coastal area

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Abstract

The analysis of air quality data in a monitoring site in the southern part of the Apulia region (south-eastern Italy) has shown that it exceeds the daily mean value of particulate matter with an aerodynamic diameter less than 10 μm (PM10) established by Italian regulations in force. In the neighbourhood of the site relevant power plants are present. The aim of this study is to evaluate the contribution of these industrial sources using the RAMS [1]-CALMET [2]-CALPUFF [3] modelling system.

Results show that the contribution of industrial sources is significant to the total pollution, but such a contribution explains only a small percentage of the PM10 measured in the site. The fallout of primary particulate matter has turned out very low, while the contribution of the secondary one, related mostly to SO_x and NO_x emission, has been higher. Meteorological and dispersion simulation indicate that the high values registered in the site can be attributed to a local source present in the little town where the station is placed and are representative of a very small area.
Keywords: industrial sources, particulate matter, wind calm.

1 Introduction

The atmospheric suspended particulate matter represents one of the most well-known environmental problems in the industrial countries, such as Italy. A recent study of the Italian Committee for Air Pollution [4] analyzed the characteristics of particulate pollution, especially that with an aerodynamic

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diameter less than ten micrometer (PM10), which represents the most dangerous fraction for human health and it is regulated by National and European law.

Anthropogenic prime sources of PM10 are combustion, vehicular traffic and industrial processes. Concentration levels of airborne pollutants within a city depends on many factors of which the most important are the strengths and the distribution of local pollution sources, presence of distant pollution sources that have impact on the city, and meteorological and topographical conditions of the area. Moreover, it must be noted that particulate matter doesn't come exclusively from direct emission (called "primary"), but it forms through complicated chemical-physical mechanisms ("secondary") starting from gaseous elements such as nitrogen oxides (NO_x) and sulphur oxides (SO_x).

As emerged by the previously mentioned study, the contribution of secondary PM10 to the total concentration is relevant, such to be determining in the episodes of exceeding the daily mean value as established by Italian regulation in force (50 $\mu g/m^3$). This is why, in the presence of primary PM10 sources produced by combustion and gaseous precursors of secondary PM10, it's important to follow the plume evolution of both pollutants for better understanding the ground measurements of the air quality monitoring stations.

Specific studies should be carried out to evaluate environmental impact [5] of pollutants in the study area, due to a combination of causes: the presence of huge industrial plants, in particular power plants whose combustion processes gives rise to the emission of both primary and gaseous precursors of secondary particulate pollutants; emission of pollutants depends on combustion matter's quality and technology; transport, transformation and deposition of contaminants depends on regional climatic conditions.

The present work focuses on the study of PM10 concentrations registered in a coastal region and the relationship with the power plant emissions, in particular the contribution of secondary component to the total ones.

2 Description of the area

The investigated area is located in south-eastern Italy, washed by the Adriatic Sea on the eastern side and by the Ionian Sea on the western. It is long and narrow with a topography generally flat such to have a weak effect on the flow: the region is influenced along its entire coastal perimeter, mainly by complex sea-land breeze systems caused by the diurnal heating cycle.

Figure 1 shows the domain of interest: there is an Air Force meteorological station (MET1), a meteorological station belonging to the University of Lecce (MET2), and the monitoring site AQ1 situated in the small town of Torchiarolo, that measures both meteorological and air quality data.

This station is classified as a background industrial station, even if, compared with this classification, its location seems to be not so good: in fact it is located in a light sinking, close to the town in the W-SW direction, that creates a kind of barrier as well as being itself an emission source of pollutants.

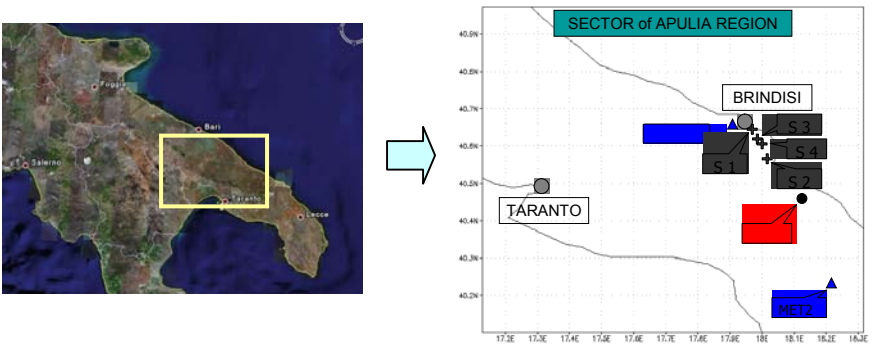

Figure 1: Study area; (on the right) black point is the AQ1 air quality station, the triangles are the meteorological stations of Air Force near Brindisi (MET1) and University of Lecce (MET2), and the crosses (S1/S4) are the industrial point sources.

The PM10 measurements carried out during 2005 in site AQ1 have shown they exceed the daily mean value, particularly in the winter season (Figure 2). In the area there some important industrial plants, in particular power plants.

They emit into the atmosphere primary fly ash particles and secondary aerosol which are carried and dispersed by atmospheric motion over a wide range, depending on the various meteorological parameters. In particular the gas-to-particle conversion process gives rise to considerable volumes of highly reactive secondary particulate pollutants after the oxidation of sulphur and nitrogen oxides. Bearing in mind these processes, in power plants with high SO_2 and/or NO_x emission, the generation of secondary particulate could reach up to a few orders of magnitude higher than those of primary particulate emissions, in mass per year.

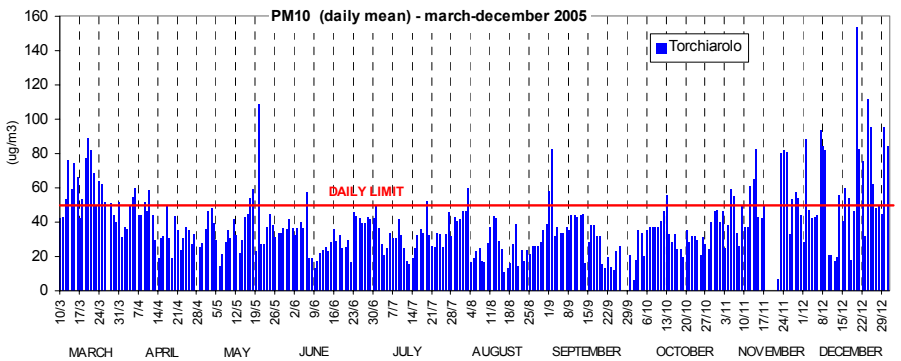

Figure 2: Daily mean concentrations of PM10, measured at site AQ1 during 2005.

In Table 1 the geometrical characteristics and the emissions of the industrial sources considered in the case studies are summarized.

Table 1: The geometrical characteristics and the emissions of the industrial sources.

INDUSTRIAL SOURCES	STACK HEIGHT (m)	SO_2 (t/a)	NO_x (t/a)	PTS (t/a)	FUEL
S1	60	2.238	3.272	152	COAL
S2	200	11.860	9.970	1.052	COAL
S3	50	3.600	1.915	133	OIL
S4	53	1,6	26	1,1	WASTE

Due to the combination of synoptic circulation regime and local features, meteorology of the area is quite complex: the wind field is characterized by a great temporal variability and all the area is subject to complex land-sea-land circulation system.

Figure 3 shows the wind roses calculated in the meteorological station MET1 (Figure 3(a)) and MET2 (Figure 3(b)), and station AQ1 (Figure 3(c)), all equipped with instruments for measuring wind intensity and direction. A prevailing NW component is observed in all stations; in the first two (MET1-MET2) a strong S-SE component is also evident, while in the third (AQ1) the wind direction is much more distributed.

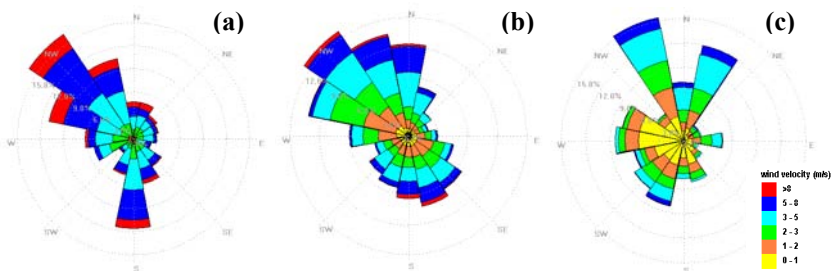

Figure 3: Wind roses measured in the MET1 station (a), in MET2 station (b) and in AQ1 station (c).

At AQ1 station the wind intensity of about 0-1 m/s represents almost the 40% on the total wind rose, especially along the western direction, while the percentage of wind calm is about 24%. On the contrary, the meteorological stations MET1 and MET2, even keeping almost the same direction, have a calm percentage from 1% to 9%. By comparing AQ1 station with the other two, it is

evident that the houses all around the monitoring site represent a kind of shield to the anemometer placed in the station.

The high number of calms has important consequences on the distribution of pollutants that arrive and develop there.

3 Modelling set up

The modelling system includes two meteorological models, RAMS and CALMET, and a dispersion model, CALPUFF. This model cascade suits quite well in describing specific situations with topographical and meteorological unhomogeneities [6], such as sea breezes, with computational domain from tenth of meters to hundreds of kilometers, times of average from hour to year, point sources, presence of inert pollutants or characterized by linear chemical conversion and removal processes.

The meteorological prognostic model RAMS (Regional Atmospheric Modelling System), developed at Colorado State University, is able to reproduce local circulation by means of a grid computation nesting, with a growing resolution. It contains an atmospheric model, which performs the actual simulation and a data analysis package which prepares initial data for the atmospheric model from observed meteorological data. The atmospheric model is constructed around the full set of primitive dynamical equations, which govern atmospheric motions. The RAMS model in this study was initialised and driven using the data from the European Centre for Medium-Range Weather Forecasts (ECMWF), updating fields every six hours; it has ran with a grid configuration of 3 nested grids, as shown in Figure 4, able to simulate meteorological driving forces at different spatial-temporal scales [7].

CALMET (CALifornian METeorological model) is a meteorological model which includes a diagnostic wind field generator containing objective analysis and parameterized treatments of slope flows, kinematical terrain effects, terrain blocking effects, a divergence minimization procedure, and a micro-meteorological model for overland and over water boundary layers.

CALPUFF (CALifornian PUFF model) is a non-steady-state Gaussian puff model containing modules for complex terrain effects, over water transport, coastal interactive effects, building downwash, dry and wet pollutant removal, and simple chemical transformation. It is designed to use meteorological fields provided by CALMET and time-dependent source and emission data. It produces one-hour averaged ground concentrations for the simulated chemical elements.

It is particularly suggested in estimating primary pollutant concentrations, but it contains a module that treats, in a simple way, some reactions of first order and that consists of a five species' scheme (SO_2, SO_4, NO_x, HNO_3, NO_3) based on the chemical mechanism MESOPUFFII [8]. The choice of this model is justified by the short availability of emission data, especially related to the speciation of particulate matter.

The characteristics of the modeling system are summarized in Table 2.

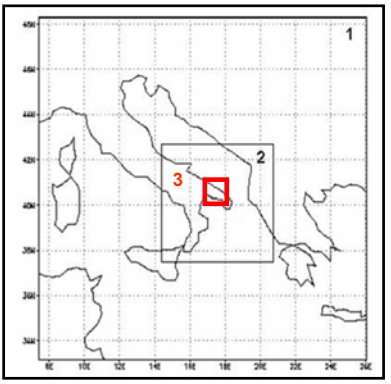

Figure 4: Grid structure for the simulations.

Table 2: Set up of modelling system.

MODELLING SYSTEM	RAMS	CALMET	CALPUFF
Grids	Grid 1: 26x26x25 - Δx=Δy=36 km Grid 2: 30x30x25 - Δx=Δy=9 km Grid 3: 50x50x25 - Δx=Δy=2 km	Grid 3: 50x50x10 Δx= Δy=1km	Grid 3: 50x50x10 Δx= Δy=1 km
Options	Meteorological updating fields from ECMWF	Interpolation of prognostic wind field. No-obs option	Chemical mechanism MESOPUFF

Two representative cases have been chosen that are characterized by the meteorological condition in which AQ1 station is downwind to the emission sources for some hours and it measures those exceeding the daily mean value of PM10. In Table 3 the scheme of case studies is shown.

Table 3: Scheme of case studies.

CASE STUDIES	PERIOD
Case A	13-16 October 2005
Case B	11-14 November 2005

4 Results and discussion

To verify the capability of the models to reproduce meteorological features of the area a comparison between meteorological model results and measurements has been performed.

Figures 5 and 6 show comparisons of the observed and predicted wind speed and direction values, during the two case studies. For all the stations, a diurnal wind cycle with more or less pronounced variability is evident.

In both cases the model is able to reproduce in a realistic way the wind field: when wind flows from western sectors the data registered in AQ1 are less than the modelled ones, confirming the fact that this monitoring station is strongly influenced by the presence of houses all around in the western, south-western sides.

In addition, it must be kept in mind that comparisons between observations and model predictions are complicated by the fact that observations are point measurements, while model predictions are representative for a horizontal grid cell of 1000 x 1000 m.

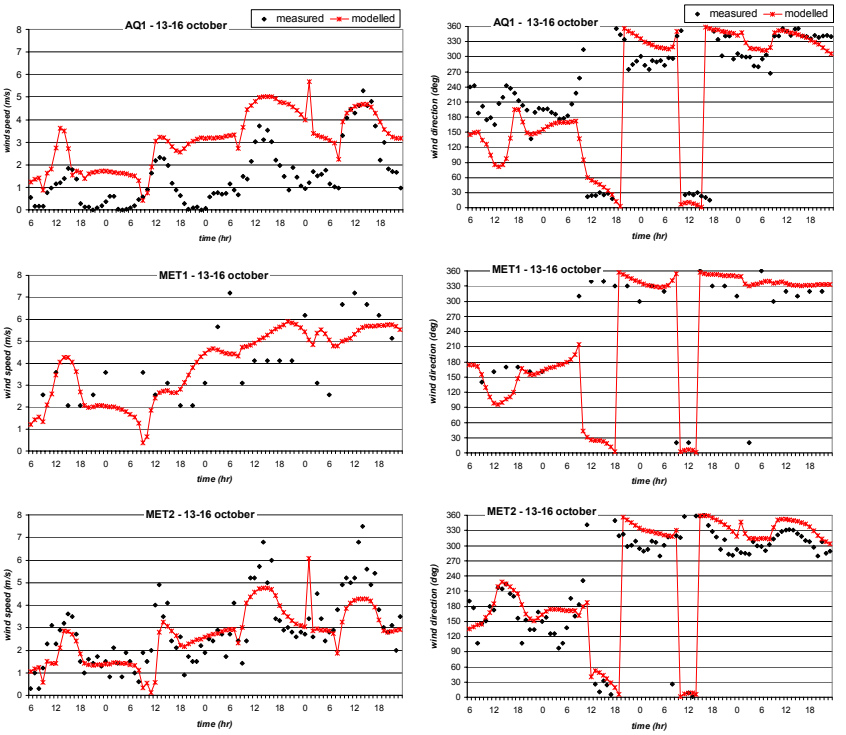

Figure 5: Evolution of modelled (line) and observed (point) hourly average wind speed (left) and direction (right) at the three stations, 13-16 October 2005.

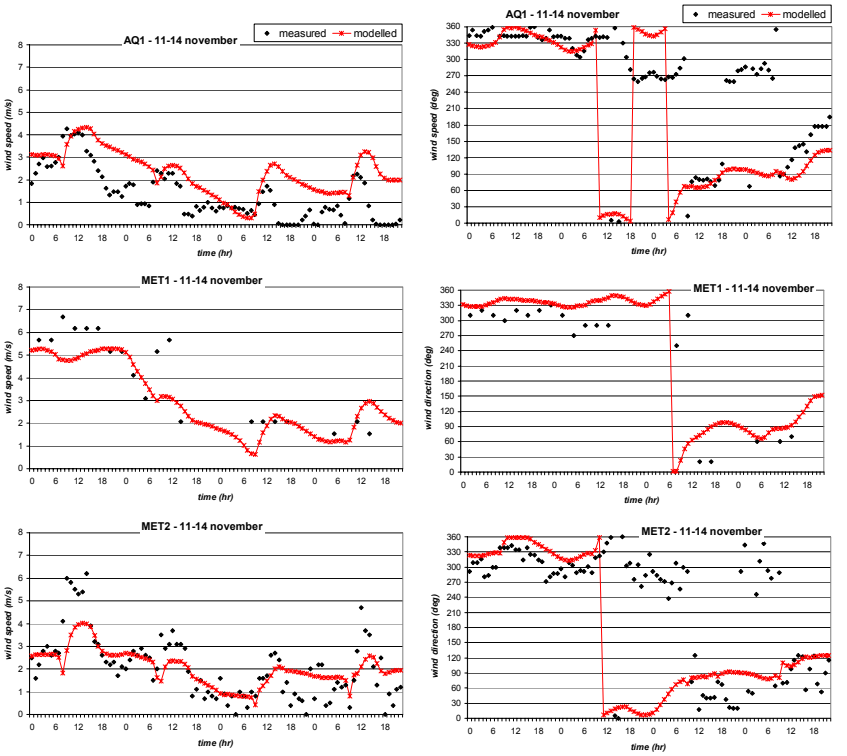

Figure 6: Evolution of modelled (line) and observed (point) hourly average wind speed (left) and direction (right) at the three stations, 11-14 November 2005.

In Figure 7 concentration fields (hourly averages at ground level) of primary (left panels) and secondary (right panels) particulate matter (as the sum of nitrates and sulphates) are shown for a specific day characterized by northern prevalent wind direction.

Fields are the sum of impact of each of the four industrial sources considered. The concentration values of secondary particulate seem to be always higher, sometimes of an order of magnitude, than the primary ones. The sum of primary and secondary components, averaged on 24 hours, is however well below of PM10 daily values measured during the two periods in station AQ1, representing just the 10-20%.

The lack of speciation data of both emitted particulate and other emission sources does not permit to estimate the contribution of other secondary components.

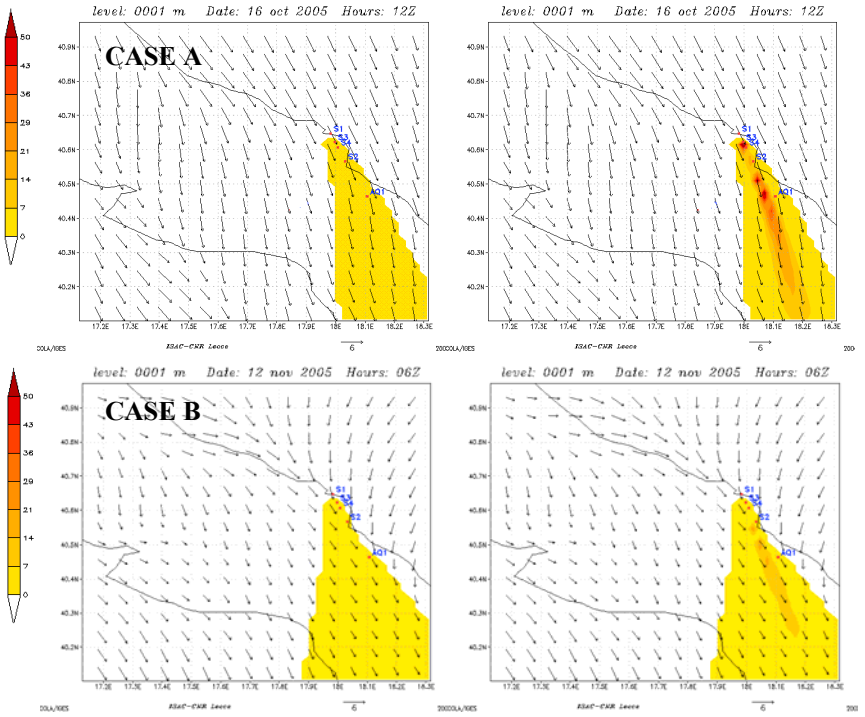

Figure 7: Ground concentration fields (μg/m^3) of primary (left) and secondary (right) PM10 for the two study cases.

5 Conclusions

In order to estimate the contribution of industrial sources exceeding the daily mean value of PM10 measured in the air quality monitoring station of AQ1, the RAMS-CALMET-CALPUFF modelling system has been used, for reproducing both meteorology and the dispersion of primary and secondary particulate matters. Modelling results have been compared with measured data. Results indicate that: i) the contribution of industrial sources to PM10 is present but it can explain just a little percentage of PM10 measured in AQ1 (10-20%); ii) the fallout of primary PM10 turns out lower than secondary component related mainly to the emission of SO_x and NO_x gaseous precursors; iii) the high number of calms registered in the station are strictly related to the particular positioning site of the station, so the high PM10 values can be related to emissions coming from the town and are not representative of the area.

Acknowledgements

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A neural network based model to forecast hourly ozone levels in rural areas in the Basque Country

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Abstract

The goal of this work is to build and evaluate a multilayer perceptron based model to forecast tropospheric ozone (O_3) levels, in real-time, up to eight hours ahead at two rural stations located in the Autonomous Community of the Basque Country (North Central Spain). Current and historical hourly concentrations of ozone, nitrogen dioxide (NO_2) and meteorological variables were used to determine the input variables of the model. The designed basic model established sixteen multilayer perceptrons, which were trained using the scaled conjugate gradient algorithm. The performance of the model was evaluated using the statistics of the Model Validation Kit. The study proved the capability of artificial neural networks to forecast efficiently ozone concentrations at rural stations in the Basque Country.
Keywords: multilayer perceptron, artificial neural networks, air quality modelling, ozone.

1 Introduction

The pollution caused by photochemical oxidants is one of the main problems in air quality. In this way, the tropospheric ozone (O_3) must be considered as a relevant air pollutant. The tropospheric ozone is a secondary pollutant, originated

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as a consequence of the reactions produced among the nitrogen oxides (NOx) and the volatile organic compounds (VOCs) under the solar radiation. Based on the data registered in the Air Quality Monitoring Network of the Basque Government, it is known that high O_3 concentrations were recorded at rural stations such as Pagoeta and Valderejo, and high ozone concentrations have adverse effects on human health and the environment. Consequently, the short-term prediction of O_3 would be very helpful. Therefore, the goal of this work is the elaboration and validation of a prediction model to forecast, in real time, hourly O_3 concentrations up to eight hours ahead at rural stations.

In the last decades cause/effect models and statistical models have been developed with the purpose of forecasting O_3 hourly levels [1]. Recently, the artificial neural networks have become very useful in the elaboration of prognostic models to forecast air quality levels [2, 3]. The artificial neural networks have proved their efficiency to describe non-linear relationships such as those involved in ozone formation, and they have generally provided better results than linear methods [4, 5].

Our research team has elaborated and evaluated a prognostic model, based on the use of artificial neural networks, to forecast in real time hourly ozone concentrations up to eight hours ahead at several stations of the Air Quality Monitoring Network of the Basque Country. This paper shows the results obtained at two rural stations named Pagoeta and Valderejo.

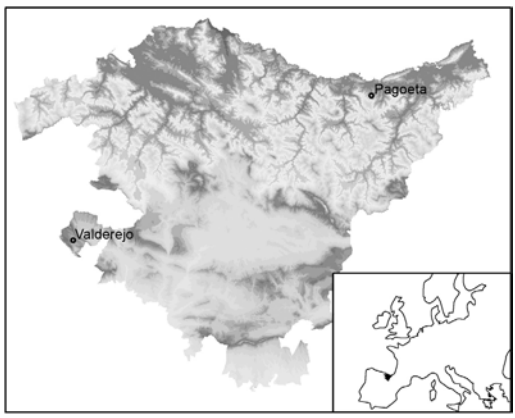

Figure 1: Pagoeta and Valderejo stations.

2 Database

The Air Quality Monitoring Network of the Autonomous Community of the Basque Country measures hourly several meteorological parameters and air pollution variables at each station. The database considered in this work is formed by the hourly measures of tropospheric ozone (O_3), nitrogen dioxide (NO_2), temperature, relative humidity, pressure, solar radiation, wind speed and

wind direction registered during the period 2001-2004 at Pagoeta (lat.: 43º15´2´´, long.: 2º9´18´´, alt.: 215) and Valderejo (lat.: 42º52´31´´, long.: 3º13´53´´, alt.: 911). Pagoeta is located on the coast of the Basque Country and Valderejo is situated in the SW of the Basque Country, approximately 97 km away from Pagoeta (Figure 1).

3 Methodology

3.1 The multilayer perceptron

The artificial neural networks are structures similar to the nervous human system, where the neuron is the fundamental element. Depending on the structure and connections, the characteristics of the neurons and the learning algorithm of the artificial neural network, there are different types of artificial neural networks. The multilayer perceptron (MLP) is the artificial neural network with the biggest number of practical applications.

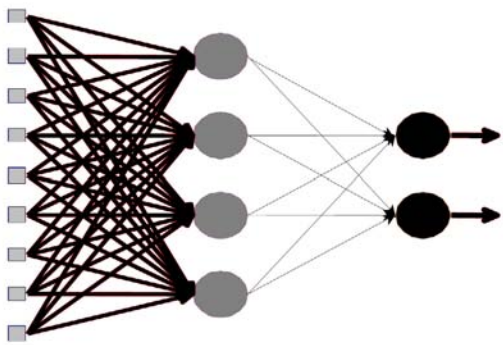

Figure 2: The 9-4-2 multilayer perceptron.

Figure 2 shows a multilayer perceptron with 9 neurons in the input layer, 4 neurons in the hidden layer and 2 neurons in the output layer. The multilayer perceptron consists of at least three layers: the input layer, the hidden layer(s) and the output layer. The input layer receives the information that enters from the outside to the artificial neuronal network. This information propagates towards ahead, so that each input is multiplied by the synaptic weights and the total sum of the products is connected to each neuron of the hidden layer. A transfer function is applied to this sum and the result becomes the input of the following layer. The multilayer perceptron could be formed by one or more hidden layers. Finally, the output layer produces the output of the multilayer perceptron.

The artificial neural networks, and in particular the multilayer perceptron, possess the aptitude to learn from the patterns introduced to them and the error

measured in the learning process, so that finally they are capable of identifying a pattern never seen previously. Consequently, it is said that an adequately trained artificial neural network has high generalization capability. The learning procedure is equivalent to the minimization process of the error

$$E = \frac{1}{S}\sum_{k=1}^{S}(t_k - y_k)^2 \tag{1}$$

observed between the target $(t_1, t_2, ..., t_S)$ and the output $(y_1, y_2, ..., y_S)$ of the neural network, where S is the number of training patterns. The output of the multilayer perceptron is compared to the target, and the error is propagated backward through the network to produce an adjustment in the weights and biases of the network, so that the difference between the output of the network and the target is minimized. Once the minimum of the difference has been reached, the learning finishes. This method is known as backpropagation.

3.2 Building the model

The multilayer perceptron based models built in this work have the structure N-L-1, with N neurons in the input layer, L neurons in the unique hidden layer and one neuron in the output layer, which corresponds to the prediction of ozone at time $t+k$ or output of the model $O3(t+k)$, being $k = 1, \ldots, 8$.

The inputs of the model were determined by stepwise regression and tolerance filtering using data from 2001-2002. In this manner, the number of input variables was reduced, being the ozone concentration at the prediction time, $O3(t)$, the variable that explained the biggest percentage of the variance in the prediction models to forecast ozone concentrations at time $t+k$, ($k = 1, \ldots, 8$) at Pagoeta and Valderejo. Past values of the solar radiation and wind direction variables played also a significant role as input variables in these prognostic models. In the same way, taking into account the importance of the utilization of seasonal components as predictors to forecast hourly ozone levels, the variable $\cos(2\pi h/24)$ was considered as another important input variable. Therefore, the general structure of the prognostic model was N-L-1, with $N = 3, 4, 5$. The number of neurons in the hidden layer L was calculated by a generalization rule [6] applied in a trial and error procedure.

The training algorithm used was the scaled conjugate gradient (SCG) algorithm; it is a variation of backpropagation that provides generally better results and a faster convergence [7]. Moreover, in order to avoid overtraining, the early stopping technique was applied, by dividing the whole database into three subsets: data from the period 2001-2002 formed the training set, data from 2003 formed the validation set and the test set was formed by data from year 2004. The validation set is used to guarantee the generalization capability of the model. It indicates the stop of the training, before the error on the validation set begins to rise.

The hyperbolic tangent function *tansig(x)* was considered as the transfer function between the input layer and the hidden layer and the linear function *lin(x)* connected the hidden layer and the output layer.

$$tansig(x) = \frac{e^{x} - e^{-x}}{e^{x} + e^{-x}} \tag{2}$$

$$lin(x) = x \tag{3}$$

Finally, eight multilayer perceptrons were set to forecast the values of the variables *O3(t+k)* at each station of the study, being $k = 1, 2, \ldots, 8$.

3.3 Goodness of the fit

Once the prognostic model was built, the statistics of the Model Validation Kit were chosen to determine the goodness of the fit of each ozone prediction [8]. These are the proposed measures in the Model Validation Kit: (i) the correlation coefficient

$$R = \frac{\overline{(C_o - \overline{C}_o)-(C_p - \overline{C}_p)}}{(SC_p)(SC_o)};$$

(ii) the Normalized Mean Square Error,

$$NMSE = \frac{\overline{(C_o - C_p)^2}}{(\overline{C_o})(\overline{C_p})};$$

(iii) the factor of two, *FA2,* which explains the ratio $0.5 \le C_o/C_p \le 2$;
(iv) the Fractional Bias,

$$FB = 2\frac{\overline{C_o} - \overline{C_p}}{\overline{C_o} + \overline{C_p}};$$

and (v) the Fractional Variance,

$$FV = 2\frac{SC_o - SC_p}{SC_o + SC_p}.$$

The notation in use in these terms is the following one: C_o is the observed concentration of ozone, C_p is the prediction, $\overline{C_o}$ and $\overline{C_p}$ are the mean values and SC_o and SC_p are the standard deviations of C_o and C_p respectively.

Based on the values of the statistics of the Model Validation Kit, the best forecast is that whose *NMSE, FV* and *FB* values are zero and the corresponding values of *R* and *FA2* are the unit.

4 Results

In this study, the calculation of the statistics of the Model Validation Kit on the test set (year 2004) determined the goodness of the fit of the prognostic model designed to forecast ozone concentrations up to eight hours ahead. The values

presented in Table 1 prove the accuracy of the ozone predictions obtained as outputs of the designed models at Pagoeta and Valderejo.

Furthermore, the accuracy of the model could be graphically observed as in the example presented from Figure 3 to Figure 10, where the ozone forecasts up to eight hours ahead were calculated at time t (t = 1, 2, …, 24) with data of 4 August 2004 at Pagoeta. In these figures the solid lines represent the real ozone concentrations (observations) and the dotted lines depict the ozone forecasts (outputs) at time $t+k$, being k = 1, 2,…,8.

Table 1: Statistics of the Model Validation Kit at Pagoeta and Valderejo on the test set (year 2004).

	NMSE	*R*	*FA2*	*FB*	*FV*
O3pago(t+1)	0.0007	0.9969	0.9978	-0.0023	0.0468
O3pago(t+2)	0.0032	0.9840	0.9964	-0.0007	0.1061
O3pago(t+3)	0.0046	0.9792	0.9932	-0.0036	0.1556
O3pago(t+4)	0.0077	0.9690	0.9926	-0.0024	0.2376
O3pago(t+5)	0.0090	0.9611	0.9905	-0.0003	0.2487
O3pago(t+6)	0.0104	0.9599	0.9912	0.0049	0.2953
O3pago(t+7)	0.0117	0.9543	0.9895	0.0006	0.3194
O3pago(t+8)	0.0138	0.9360	0.9901	0.0030	0.3166
O3valde(t+1)	0.0010	0.9965	0.9998	0.0100	0.0408
O3valde(t+2)	0.0045	0.9851	0.9884	0.0211	0.1131
O3valde(t+3)	0.0183	0.9216	0.9926	0.0384	0.1530
O3valde(t+4)	0.0198	0.9237	0.9926	0.0430	0.2318
O3valde(t+5)	0.0293	0.8751	0.9862	0.0403	0.3057
O3valde(t+6)	0.0221	0.9510	0.9871	0.0248	0.4571
O3valde(t+7)	0.0491	0.8729	0.9770	0.0665	0.7184
O3valde(t+8)	0.0736	0.7592	0.9582	0.0773	0.9800

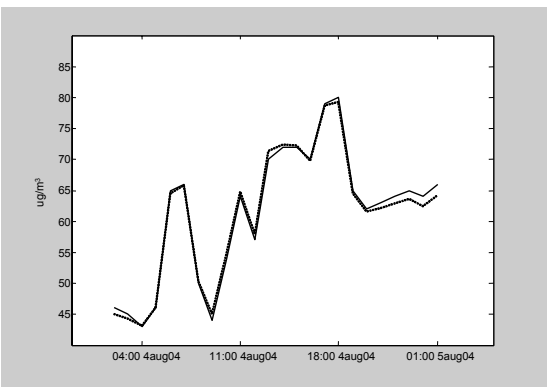

Figure 3: Observation and output *O3(t+1)* at Pagoeta with data of 4 August 2004.

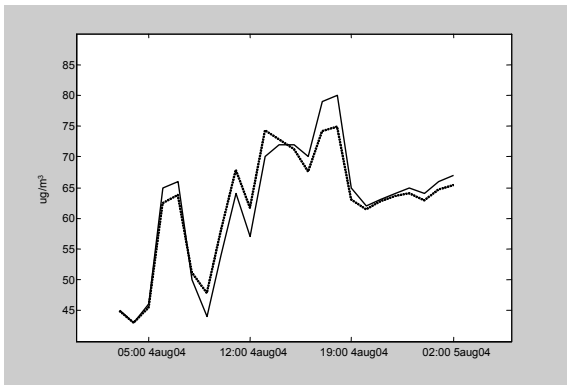

Figure 4: Observation and output *O3(t+2)* at Pagoeta with data of 4 August 2004.

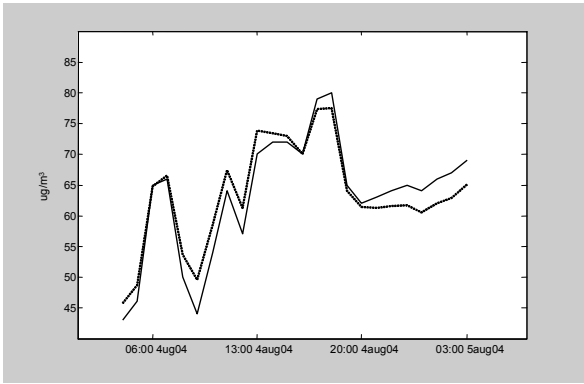

Figure 5: Observation and output *O3(t+3)* at Pagoeta with data of 4 August 2004.

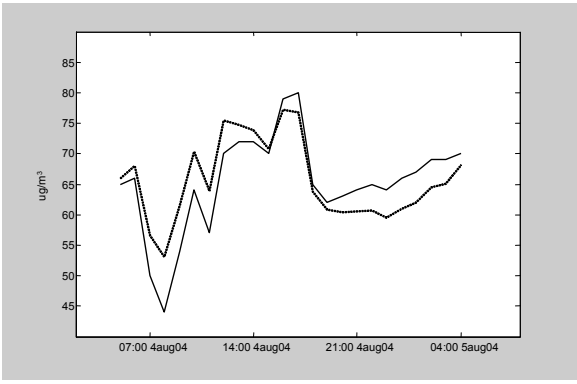

Figure 6: Observation and output *O3(t+4)* at Pagoeta with data of 4 August 2004.

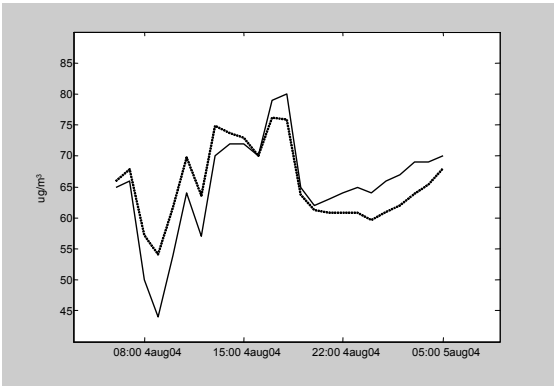

Figure 7: Observation and output *O3(t+5)* at Pagoeta with data of 4 August 2004.

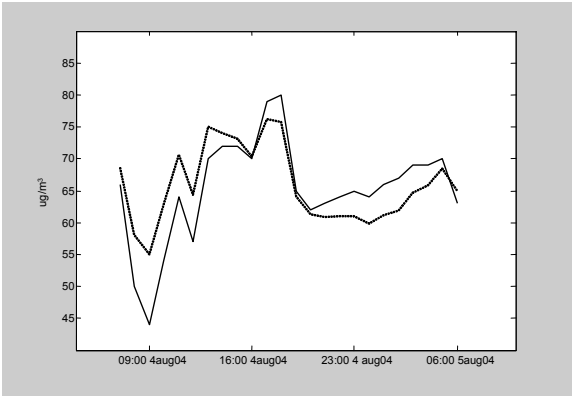

Figure 8: Observation and output *O3(t+6)* at Pagoeta with data of 4 August 2004.

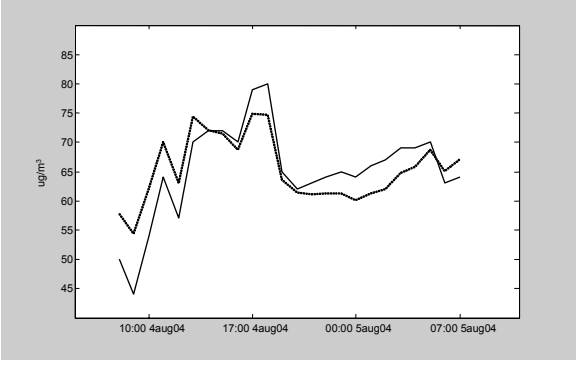

Figure 9: Observation and output *O3(t+7)* at Pagoeta with data of 4 August 2004.

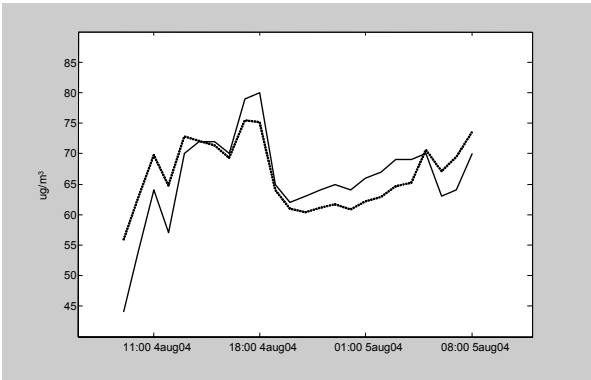

Figure 10: Observation and output *O3(t+8)* at Pagoeta with data of 4 August 2004.

5 Conclusions

In the present work, a multilayer perceptron based model was used to forecast hourly ozone concentrations up to eight hours ahead at two rural stations in the Basque Country, named Pagoeta and Valderejo. A joint study of the values of the statistics of the Model Validation Kit proved the efficiency of the designed model, which performed in the same way at these two rural stations, independently of its location. The model was also successful in other rural and urban stations on the coast of the Basque Country.

Acknowledgement

The authors in this study, the calculation of the statistics of the Model Validation Kit on the test set determined the goodness of the fit of the LR, MLP1 and MLP2 models in a quantitative manner, wish to acknowledge the Environmental Department of the Basque Government for providing data from the air pollution network and for their financial support to realize the present study.

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Satellite imagery used in constructing emission maps for air quality modelling in the Dubai-Sharjah (UAE) region

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Abstract

Streamlined construction of emissions maps using satellite imagery (JPEG - RGB images) is discussed. A filter algorithm (MATLAB) is used to extract a road network which is subsequently used as an input to a "fast" (reduced-order) urban air shed model for the Dubai-Sharjah (UAE) region. Validation of the model is done using averaged air quality scenarios in an extended (one month) campaign, revealing that O_3 production is VOC limited in mid to late afternoon (peak ozone times). The modelled NO_x and O_3 concentrations are in rough agreement with the three measuring stations used in this study (two in the city center and one at the city periphery); high O_3 levels are predicted down-wind (desert-side) of the Dubai-Sharjah city centers in mid-afternoon.
Keywords: air quality, reduced-model, ozone, NO_x, VOC, optimization.

1 Introduction

The Dubai-Sharjah (UAE) metropolitan region, henceforth DS, covering approximately 15×60 km^2, represents one of the world's and fastest growing major metropolitan areas. The rapidly evolving transportation infrastructure has demanded that an efficient algorithm be developed which could be an alternative to the arduously constructed road networks using GIS traffic management software. The non-linear O_3 production from precursor gases NO_x and VOC is extremely CPU intensive and thus created the necessity for the fast ozone calculator TAPOM-

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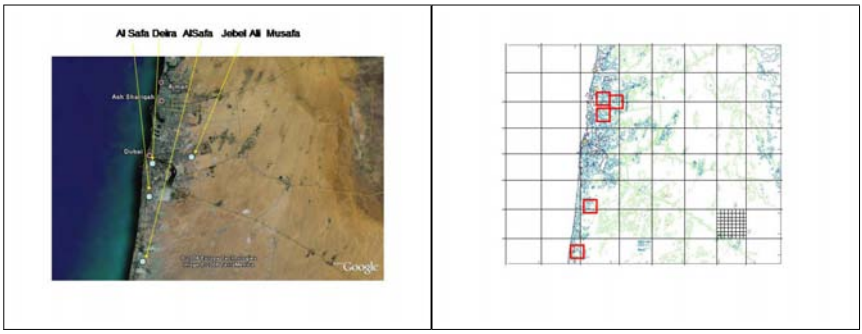

Figure 1: Satellite image (Google-Earth, public online software)) transformed to a colored bitmap mesoscale emissions image for the DS metropolitan region. The 30×30 km^2 and 500×500 m^2 (lower right example). The thick red boxed regions represent the industrial emissions area.

Lite, hereby referred to as TL. (An adaptation of a 3-D photochemical dispersion model TAPOM (Transport Pollution Model).)

The emissions input (primary road networks) are required as input to TL and this report focuses on the methodology used to construct this network using RGB (Red-Green-Blue JPEG satellite images) as input to TL. This study accompanies a parallel paper [1] that explores various air quality scenarios, including a worse case scenarios using this emissions network reported here. Figure (1) shows a Google-Earth [2] ©JPEG image of the mesoscale region, the domain is centered on Latitude $25°15'$ N, Longitude $55°16'$ E. The 24-hour air quality episodes uses time steps of 1 minute and 30×30 m^2 horizontal grid spacing (at ground level) and 200m vertical grid spacing.

We proceed with a description of the use of satellite imagery for the DS region and the methodology of the road network creation (Section 2) and we follow with results of air quality modelling for the one month campaign (Section 3) and conclude (Section 4).

2 Using satellite imagery to constructing an emissions network

The total amount of NO_x and VOC present in the DS urban air-shed region was calculated using a top-down approach. The initial concentrations of the two gases used for employing this method were obtained from the database of a global emissions inventory EDGAR [3] that has been constructed for each country through a joint venture by RIVM-MNP (Netherlands), TNO-MEP (Netherlands), JRC-IES, Ispra (Italy) and MPIC-AC, Mainz (Denmark). This extensive database includes concentrations of NO_x, methane (CH4), and Non-methane VOCs produced from a variety of broad categories at the national level in units of gigagrams for the year 2000.

Five major industrial areas in the DS region are also identified and all industrial emission are modelled as emanating from the red square regions of Figure 1. The total traffic and industry emissions in tons/yr. Data from 2005 estimate, is adjusted for 2007: 129'220, 76'865, 13'716, 8577 tons/year for traffic NO_x and VOC, industry NO_x and VOC respectively (Undergraduate Thesis, B. Farooq, 2004).

The current modeling initiative in the DS region was the construction of emissions geo-spatial distributions which are divided into two parts: emissions emanating from *traffic* and *industrial* sources. Most NO_x sources come from line sources (traffic) and VOC from area sources (e.g. gas stations) [4], suggesting that a model using an image of the region would mimic the distribution of these sources. The region's rapidity evolving traffic infrastructure called for an innovative way to model the emission line sources; thus a major development presented here is the construction of an emission network from traffic using satellite imagery and to a lesser extent, the modelling of industrial emissions. This initiative converted a digital satellite image (Figure 1), to a matrix map of the region, with resolution 30×30 m^2 (Figure 2). The O_3 concentrations calculated by TL are then compared to the actual measured concentrations at the locations of the monitoring stations in Dubai.

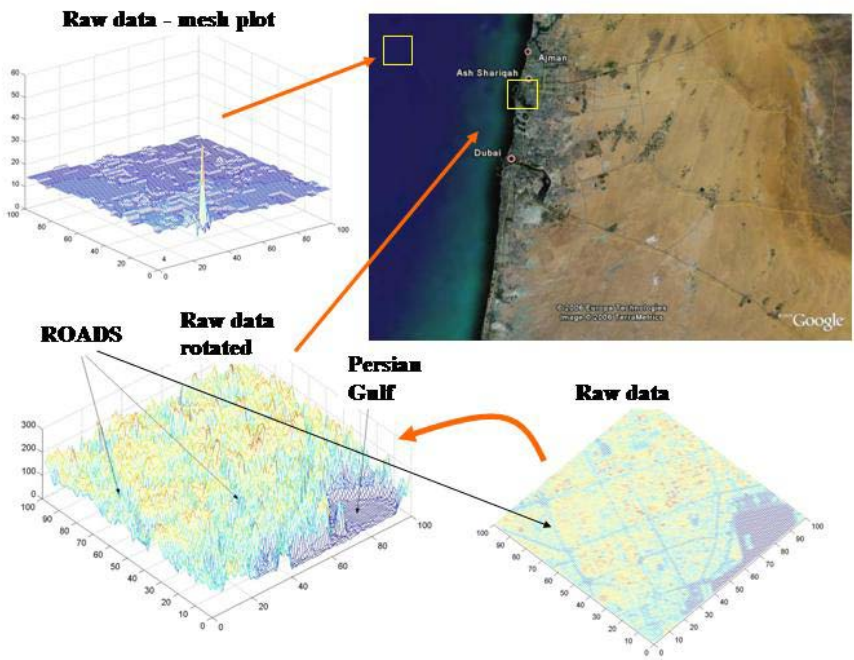

Figure 2: Examples of RGB [0,255] segmented bitmap transformed JPEG image of the DS region: (upper left) sea and (lower left) land. Also shown is the image rotated and viewed from above (lower right) [1].

A 1300×1000 pixel bitmap (RGB colorspace) of DS was created from a JPG formatted image. The traffic emission are treated using a simple algorithm, a MATLAB © command `imread`, used to extract the image (originally $30 \times 30\ \mathrm{km}^2$) to a digital format of resolution $30 \times 30\ \mathrm{m}^2$. The created images has assigned numbers ranging from [0,255] that represent the shades and colors of the original image. Roads were empirically identified as the RGB color code between ($50 <$ RGB < 80) and water or sea as RGB color code ($0 <$ RGB < 30), we refer to as SEA (Figure 3, lower left). A simple algorithm was used to distinguish roads from all other surface features. Defining the current grid in the image as $CG(x, y)$ in Cartesian coordinates, $x \in (1, 1300)$, $y \in (1, 1000)$ (grid or pixel space), the following conditions had to be satisfied in order that the grid was identified as road (RD) and not as a false "road" artifact (NRD), building, land or sea.

condition	action
$CG(x, y) \in RD$	CONDITION 1
$CG(x \pm 1, y) \in RD\ OR\ CG(x, y \pm 1) \in RD$	CONDITION 2
$CG(x \pm 1, y \pm 1) \in RD\ AND\ CG(x\mp, y \pm 1) \in RD$	CONDITION 3
$CG(x \pm 1, y) \notin SEA\ AND\ CG(x, y \pm 1) \notin SEA\ AND$	
$CG(x \pm 1, y \pm 1) \notin SEA\ AND\ CG(x\mp, y \pm 1) \notin SEA$	CONDITION 4
$CG(x \pm 2, y) \notin SEA\ AND\ CG(x, y \pm 2) \notin SEA\ AND$	
$CG(x \pm 2, y \pm 2) \notin SEA\ AND\ CG(x\mp, y \pm 2) \notin SEA$	CONDITION 5

The conditions are defined in the following way: Condition 1 - pixel is identified as road, Condition 2 - adjacent pixel on image axis is identified as road, Condition 3 - pixel on axis diagonal to image axis is identified as road, Conditions 4 and 5 - at least two pixels separate it from the SEA. If Conditions 1–5 are all satisfied, the pixel is accepted as "road" surface, otherwise it is either land or sea. The algorithm naturally identifies the width of the road and hence the type of road (with its accompanying typical traffic speeds). This algorithm was also shown to be an improvement over an earlier test explored in [1] which tested only the "on axis" grid points (Conditions 1 and 2 only) and did not contain the NRD algorithms (Conditions 4 and 5). The NRD test was a significant improvement as it helped to eliminate the false road identification due to the fall and rising slopes from sea to land in the RGB color change, clearly seen at pixels 35, 85, and 93 of Figure 3 (lower left).

An assigned road pixel, labelled $GC(x, y)^*$, must be further processed due to insufficient resolution of the JPEG picture; A resolution algorithm is therefore used to treat identified road pixels. A second treatment was applied to traffic emissions in order to take into account the lessening of traffic density away from either the Sharjah or Dubai city centers. The following weighting schemes were used,

$$f_S(x, y) = e^{-(x^2 - x_s^2)/\sigma_S^2} \cdot e^{-(y^2 - y_s^2)/\sigma_S^2} \tag{1}$$

$$f_D(x, y) = e^{-(x^2 - x_d^2)/\sigma_D^2} \cdot e^{-(y^2 - y_d^2)/\sigma_D^2} \tag{2}$$

$$CG^{**}(x, y) = CG^*(x, y) \cdot f_S(x, y) \cdot f_D(x, y) \tag{3}$$

where (x_d, y_d) represents the center grid of Dubai (Bur Dubai center, the Al-Maktoum bridge) and (x_s, y_s) represents center grid of Sharjah (Blue Souk center).

Daily emission scheduling is done in $60 \times 24 = 1440$ steps of one minute and weighted using a reasonable scheduling factor. The scheduling factor $f(t)$, is a "double-hump", $f(t) = m \cdot (t - t_o) + b_o$, increasing from midnight until morning (00:00–06:00), decreasing from morning until noon (06:00–12:00) and then repeating this pattern from 12:00 - 24:00, where $m_i = \pm 1.5/t_o$, $b_i =$

factor $f(t)$	time
$m_{night} \cdot (t - t_{night}) + b_{night}$	(00:00 - 06:00)
$m_{morn} \cdot (t - t_{morn}) + b_{morn}$	(06:00 - 12:00)
$m_{aftern} \cdot (t - t_{aftern}) + b_{aftern}$	(12:00 - 18:00),
$m_{even} \cdot (t - t_{even}) + b_{even}$	(18:00 - 24:00),

$(0.5, 2.0, -2.5, 5.0)$, $t_i =$ (0,06:00, 12:00, 18:00, 24:00) where $i \in$(night, morn, aftern, even) and $t_o = 6 \times 60$ (minutes). The combined resolution smearing and traffic weighting gives a dynamic emission map, per primary species, $E_i(t, x, y) = f(t) \cdot f_D(x, y) f_S(x, y) \cdot E_{o,i}(x, y)$, where $E_{o,i} = \int_{map} E_{o,i}(x, y) dxdy$.

3 Air quality scenarios and conclusions

The aggregated and non-speciated total VOC and NO_x are distributed using traffic network and the averaged O_3 and NO_x levels measured and simulated between the dates 11 September and 30 October 2006 are shown in Figure 5. No validation for VOC can currently be done in Dubai. Simulations were done using daily meteorology and a 24 hour spin-up time to bring the gas concentrations to acceptable levels before the actual simulation. The results of these comparison can be summarized in the following observations [1].

NO_x concentrations peak in the early morning hours, prior to 09:00, drop to a minimum in mid to late afternoons and again peak after 21:00. Partial quenching of NO_x is largely attributed to O_3 production and to a lesser part advection; between 15:00 and 18:00, NO_x levels typically drop to 10–20 ppb (at all stations) and are consistent with the increased O_3 production during this time.

O_3 concentrations peak in the late afternoon (measured) and the model predicts peaks at 12:00. Between 18:00 and 06:00, O_3 levels drop to near zero. Over advection, simplified meteorology, and the simplified NO_x and VOC scheduling in the model attributes to low levels at these times and also accounts for too early peaking of O_3. Model predictions show limited VOC available in late afternoons and contributes to low O_3 levels.

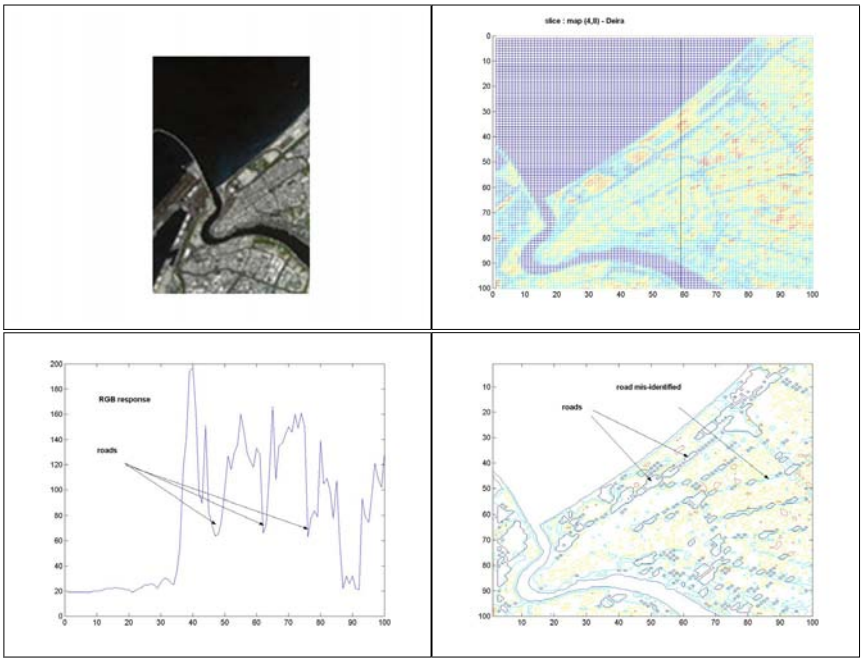

Figure 3: Deira (Dubai city center) satellite JPG image (upper left), RGB image showing image axis cut (upper right), RGB slice (lower left), filter contour plot satisfying Conditions 1–5 (lower right).

Trends in spatial evolution show the highest O_3 levels tend to be slightly downwind (desert side) of the highest road-density regions of DS (Dubia's Deira and creek-region). The high levels of ozone here indicate a need for measuring stations in regions of the air shed that are currently under-represented.

TL model was specifically designed for "averaged air quality scenarios" and is used in the integrated assessment framework of coupled models (metamodels). An example of averaged scenarios is shown in Table 1 where noontime O_3 and NO_x values are shown at the three measuring sites and compared to modeled values.

The speed of TL calculation is its strength but the "flip-side" is its weakness of accuracy, certainly at short time scales (less than one minute) and in a spatial micro view of the urban region (few 10s of meters). The inability for TL to consistently reproduce individual measurement stations is an indication of this weakness. Future improvements of the model's meteorology simulation will ameliorate this inaccuracy. (It should be noted that even the most accurate chemistry simulations and high resolution models have great difficulty in reproducing O_3 levels throughout a large urban air-shed at every point at all times.)

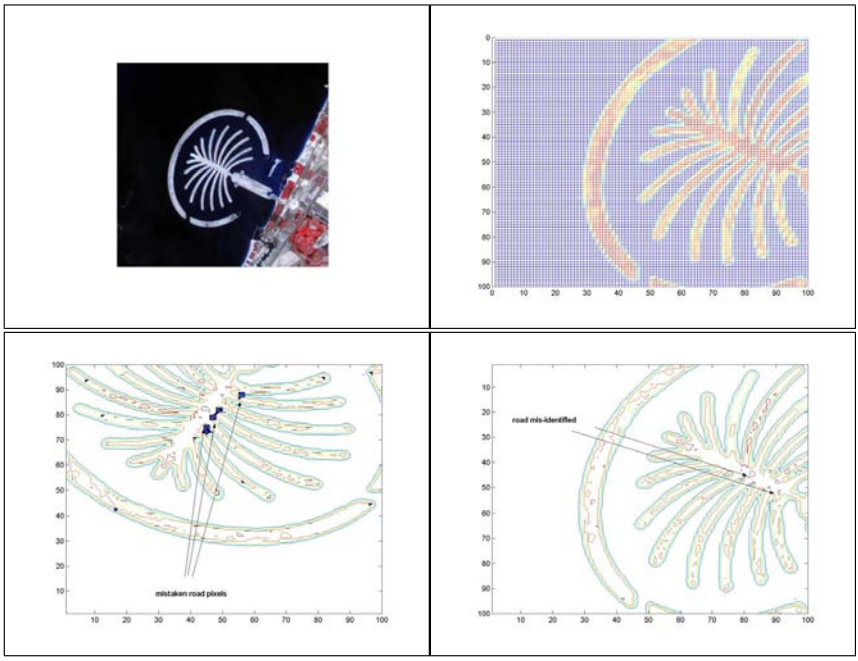

Figure 4: Palm satellite JPG image (upper left), RGB image (upper right), misidentified roads - black dots using Conditions 1 and 2 only (lower left), filter contour plot satisfying Conditions 1–5 (lower right).

4 Conclusions

TAPOM-Lite is a fast air quality calculator designed for determining trends in averaged meteorological episodes in integrated assessment work. The tool has been validated and simulations showing VOC limited O_3 production in the DS region; the lack of natural VOC sources partly explain this; O_3 peaks at midday in the simulation, approximately 3 hours earlier than measurements; simplifications in meteorology and emissions scheduling are accredited to this difference. We foresee a continued improvement on TL with the understanding that CPU costs be kept low so that the model remains viable in the optimization framework. Improvements will include a more accurate meteorology and NO_x and VOC aggregation schemes. A new application of this model is now underway for the city of Luxembourg.

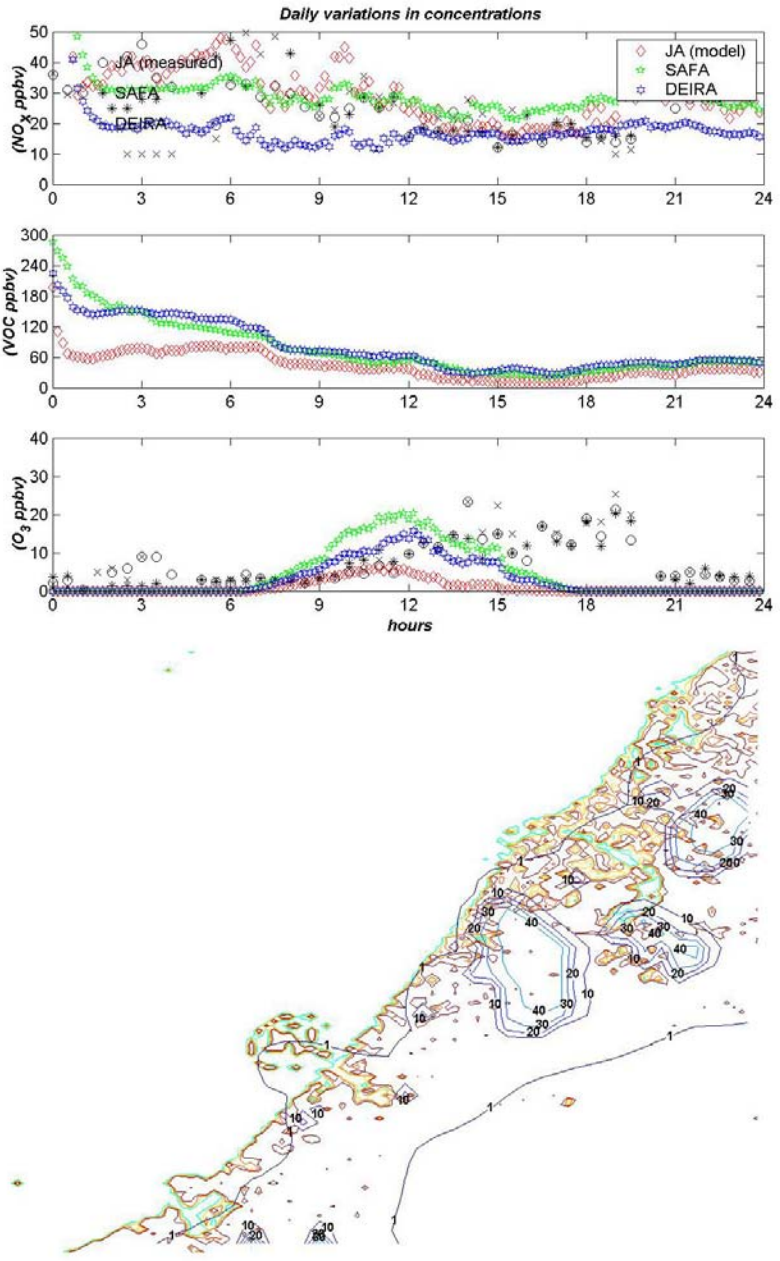

Figure 5: (a) Averaged daily variations of NO_x and O_3 (including simulated VOC) at three Dubai stations (Deira, Safa Park, and Jebel-Ali JA). Data taken from 11 September - 30 October 2006 campaign. (b) Contour plot of averaged O_3 levels at 12:00.

Table 1: Model/data comparison with measured stations on 11–15 September and averaged scenarios including extra data from 12–30 October 2006.

	Deira		Safa		Jebel Ali	
date	NO_x	O_3	NO_x	O_3	NO_x	O_3
11 Sept 06	21.1/17.7	14.9/8	33.4 /36.	24.2/4.5	34.7/26.	4.8 /10.5
12 Sept 06	15.4/12.	9.1/6	22.7 /37.	12.6/11.	20.0/23.	2.5 /6.
13 Sept 06	19.2/18.	20.1/18	30.4 /42.	25.9/7.	36.4/20.	6.5 /21.
14 Sept 06	9.2/17.	8.1/6	19.6 /18.	14.6/7.	19.2/15.	2.6 /7.
15 Sept 06	13.9/—	25.0/15	26.7/—	18.8/9.	30.6/—	4.1 /—
(*average*)	15.7/16.2	15.4/10.6	26.6/33.3	18.6/7.7	28.2/21.	4.1/11.1

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A distributed computing solution for CALPUFF

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Abstract

This paper demonstrates the skills, knowledge, and resources required for completing a refined MM5-CALPUFF analysis for a regional air quality study. The dispersion over the entire country using five years of MM5 meteorological data necessitates large scale computation. To assess additional computing resources, an intranet system developed by *Lakes Environmental* has been utilized to take advantage of idle processing cycles of all personal computers available in an organization. The distributed computing solution requires the modelling task be divided into a series of monthly calculations for each source. As partial results from participating computers are returned, they are summed to yield the final total impact in post processing. Further reduction of computational effort is achieved through application of advanced modelling techniques. Since nonlinearity of the model is insignificant for emissions involving only sulphur dioxide, as it is the case for our project, the final solution can be scaled linearly with respect to the source strength. Grouping of identical sources may also reduce some of the computation, although it is not utilized for the project. By application of innovative distributed computing solution and advanced modelling techniques, we have reduced the project life to one month, instead of one year if it were executed in a straightforward manner.
Keywords: CALPUFF, MM5, distributed computing, modelling, dispersion modelling.

1 Introduction

Recently, regulators in the U.S. have been frequently requesting more permit applicants to perform Class I area impact analyses, long range transport of pollutants, visibility studies for best available retrofit technology (BART), and

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impact evaluation of source close to the ocean. These studies involve visibility analysis, shoreline fumigation, calculation of the deposition of acidic species, and dispersion of particulate matters.

CALPUFF (Scire et al. [1]) is recommended by the U.S. Environmental Protection Agency, the Federal Land Managers Air Quality Related Values Workshop (FLAG) and the Interagency Workgroup on Air Quality Modelling (IWAQM) for evaluating Class I areas. CALPUFF, which is a non-steady-state air quality system, is issued for regulatory purposes. The emission of pollutants is simulated as a series of independent puffs. The popularity of CALPUFF has spread to the international community of environmental agencies. For instances, several Canadian provinces including B.C. and Alberta have recommended CALPUFF as a preferred dispersion model. However, the execution of CALPUFF is computational intensive and requires considerable expertise and resources. Modellers performing these analyses may require external support on several fronts, ranging from preparation of input data to the execution of the model.

As a case in point, we present our experience with a reputable client in Kuwait. The client needs to employ refined CALPUFF modelling in a manner similar to Class I area analysis. The objective is to assess the adverse effect on the environment due to emission of sulphur dioxide from a set of new power plants. This assessment begins with first evaluating the impacts from the existing sources. Subsequently, one must estimate the increase in pollution levels due to additional future sources. Furthermore, various emission rate scenarios are inspected to assess air quality as new power plants, that use various grades of fuel quality, are planned in subsequent phases. Each calculation must be performed over recent 5-year of meteorological data. Although we cannot present the results due to confidentiality, we will demonstrate the advanced skills, knowledge, and resources required to complete large scale MM5-CALPUFF simulations in this paper.

2 Preparation of meteorological data

Preparation of meteorological data is often the first hurdle for modellers, especially for international practitioners. It would be convenient to recreate the local meteorological conditions through execution of the NCAR/Penn State Mesoscale Model (MM5) (see Dudhia *et al* [2]). MM5 is primarily developed for numerical weather forecasting in regional scale. The model solves the laws of physics that govern the atmosphere. However, air quality studies employ MM5 to construct historical meteorological records, which constitute the input to dispersion models.

Figure 1 shows the MM5 domain which comprises two nested domains centred at (29.33^{o}N, 48.00^{o}E), with 23 vertical cells. The grid distances for the coarse grid and the finest grid are 36 km and 12 km, respectively, with 37 grid points in each domain. The model is executed for years between 2000 and 2004. Since the forecast spans of mesoscale models are limited to one week, the five-year execution is divided into a series of overlapping 6-day sections (e.g.

IWAQM report [3]). Each section begins with one day of repeated calculation, which is used to initialize the system. The first day output is discarded from the final dataset. Global observations are ingested into the calculations of MM5 by four-dimensional data assimilation (FDDA; see [2]). As a result, the MM5 data are able to reflect the spatial and temporal characteristics of the meteorological conditions of interest.

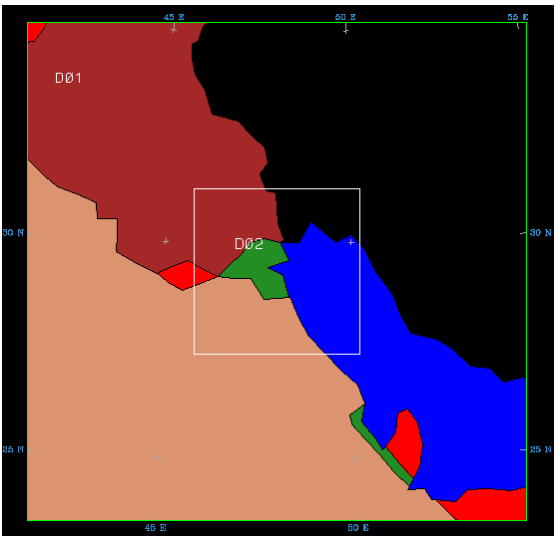

Figure 1: Two-way nested MM5 domains.

3 Execution of CALPUFF model

3.1 CALMET-CALPUFF Calculations

The CALPUFF modelling system includes a diagnostic meteorological processor known as CALMET. As a diagnostic model, CALMET does not use the full mass, momentum, and energy conversation equations. Therefore, it generally benefits from results of a prognostic model such as MM5.

The MM5 wind and temperature fields provide an initial guess field for CALMET, which creates local wind fields forced by typography or land-sea temperature contrast. The local wind fields are embedded into the guess field to produce a balance field with minimum divergence. CALMET also calculates boundary layer parameters such as mixing height and stability parameter for each horizontal grid cell. The three-dimensional meteorological field and the two-dimensional boundary layer parameters are the input to CALPUFF for further calculations.

The execution of the CALPUFF model can be intolerantly slow because it traces numerous puffs in the computational domain. A single straight 5-year (consists of 60 monthly calculations) CALPUFF simulation of the client's

project would require 80 days of computational time on a single workstation equipped with a 2.4 GHz *Intel* Xeon processor. Taking into account of all the emission scenarios, it would take 336 days for a bank of workstations with a total of 14 Xeon processors to complete calculations. A supercomputer would normally be required for such daunting computing task.

As a practical alternative to supercomputers, *Lakes Environmental Inc.* has developed an intranet system that takes advantage of the unused processing cycles of any computers over the network. This commercial system is known as HIVE Grid. To put the HIVE Grid into operation, the modelling task must be broken down into many small pieces, and the partial calculations are executed separately, joined to yield the final results. Thus, the straight CALPUFF execution is divided into a series of monthly calculations. Each run is a cold start for 3 days before the beginning of each month. These first 3 days are used to initialize the model. These three initial day results are discarded from the final monthly calculation. The monthly concentration and deposition output from CALPUFF are appended for post-processing.

3.2 Modelling techniques

In a further refinement to the distribution solution employed, each monthly calculation is modelled for one source only. The partial sums from each source are combined through the application of processor CALSUM. The advantage of separating sources is two-fold. First, each CALPUFF job will have less memory size and shorter life span. They can be conveniently fed into the PC cluster, resulting in a quick turnaround and less disturbance to co-workers, who have contributed their desktops to the computing pool. Second, the total impacts due to existing sources can be saved. The incremental impact from new sources can be added to the old impact to yield the total impact. There is no need to repeat calculations for the old sources. The reduction of computational time can be substantial, as much as 60% of CPU time in our case. The CALSUM method works because puffs are non-interacting in the CALPUFF model.

Further reduction in CPU can be achieved by source grouping. If two near sources (e.g. in the same grid cell) have identical characteristics such as stack height, stack diameter, exit momentum and buoyancy, they can be grouped as a single source with a combined emission rate. Grouping of identical sources can reduce CPU time by 8% in the case of the Kuwait project. In a more aggressive approach suggested by IWAQM ([3]), two nearby sources of similar but not exactly the same characteristics (e.g. different in stack diameter) can be grouped together as a single entity with average characteristics. This approximate method can further reduce CPU time by sacrificing accuracy. Nonetheless, source grouping has not been employed for this project.

Finally, source scaling is employed to significantly reduce the CPU time. In the project, the emission rate of each source increases linearly with respect to the percentage of the fuel's sulphur content. Table 1 shows maximum visibility, vapour concentration, amount of dry and wet deposition as a function of fuel sulphur concentration. Units in the table are arbitrary since these data are confidential. All but the visibility in Table 1 increases by the same factor

(correct to 1 decimal point) as the emission rate climbs. Backing out the background visibility constant (10 arbitrary units), the visibility parameter indeed increases by a ratio of 4.0. As in this case, the nonlinearity of the chemical transformation of sulphur dioxide is insignificant. (As it is discussed in Escoffier-Czaja and Scire [4], the chemistry of nitrous oxide has much higher nonlinear characteristics. It is important to apply POSTUTIL for repartition the equilibrium balance between ammonia nitrate and nitric acid.) The impact due to emissions from any other fuel concentrations can be linearly scaled by the source strength. The scaling factor can be implemented either at the CALSUM process or at the CALPOST process. Since there are 7 types of fuel concentrations in our project, the reduction of CPU time is 85% (or 6/7).

Table 1: Compare ratio of impacts from 4% S to 1% S for one of the emission scenarios using 5 days of MM5 data.

	Vapor			Dry deposition		Wet deposition	
	VISB	SO2	SO4	SO2	SO4	SO2	SO4
1% S	168	2.50E-4	1.52E-5	2.E-6	1.3E-9	1.38E-6	2.67E-8
4% S	640	9.90E-4	6.10E-5	8.19E-6	5.19E-9	5.52E-6	1.07E-7
Ratio	3.8	4.0	4.0	4.10	4.0	4.00	4.00

Table 2: Summary of computational processing requirements.

CALSUM	Source Grouping	Source Scaling	CPU total
No	No	No	336 days
Yes	No	No	141 days
Yes	Identical sources	No	130 days
Yes	Identical and similar sources	No	71 days
Yes	**No**	**Yes**	**21 days**
Yes	Identical sources	Yes	20 days
Yes	Identical and similar sources	Yes	11 days

Table 2 lists the estimated computational time when various modelling techniques are utilized. The bank of 14 Xeon processors is used as benchmark for estimating the total computational time. Note that the degree of CPU reduction depends on the specifics of individual project. Nevertheless, Table 2 offers insights on the relative effectiveness of each technique. The techniques applied are accepted "best-practices" for modelling over large domain and extend period. More information can be found at the IWAQM Phase 2 report [3].

For the Kuwait project, we employed the CALSUM method, source scaling without the source grouping method. Using these efficient methods, the estimated CPU time is drastically reduced from 336 days to 21 days over a bank

of 14 Xeon processors. When HIVE Grid is employed to distribute jobs over the intranet, the actual computational time can be further shortened. On the other hand, modellers have to commit more time in planning, organization, coordination, and post-processing of the data. In the end, *Lakes Environmental* completed the project in one month instead of one year.

4 Conclusion

This paper demonstrated the skills and techniques required for large scale computation of MM5-CALPUFF modelling through the execution of a typical regional air quality assessment project. The project evaluates the adverse effect of sulphur dioxide emissions from thermal power plants on air quality for varying emission scenarios. The dispersion over the entire country using five year of MM5 meteorological data necessitates large scale computation. It is estimated to take 336 days of computation for a bank of 14 Xeon processors to complete all the calculations. To avoid any delay in the project, a distributed computing solution is employed along with application of advanced modelling techniques to reduce the computational time. In this approach, the CALPUFF execution is divided into a series of monthly calculations for each single source. The partial impacts from each source are combined to yield the total impacts for various emissions scenarios. The nonlinearity of photo-chemistry is found to be negligible for emissions involving only sulphur dioxide. Therefore, emissions impact can be scaled in proportion to the source strength. This technique can eliminate overlapping emissions scenarios. Although grouping of sources may also reduce some of the computation, it is not utilized for the project. Applying efficient and inexpensive supercomputing system and "best-practices" of modelling techniques have reduced the project execution to one month instead of one year.

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Section 3
Air quality management

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Local scale vehicles pollution study in the absence of sufficient data: the case of the city of Thessaloniki

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Abstract

Air quality in urban environments can today be modelled by a large number of computer models (empirical, box models, CFD). OSPM (Operational Street Pollution Model) is one of the most widely used empirical-box models due to its simplicity and its very good performance. However, in most cases the necessary data, even for such simple computations, are not all available, leading to large errors, especially when employed for future planning. The City of Thessaloniki (Greece) was studied as an example, as although few input-data are available, there are enough measurements to validate the model's results. The current work proposes a methodology for dealing with this lack of data, confirmed by comparison with measured values. Following that, a sensitivity analysis for the most common input parameters is presented. Finally, OSPM is employed to predict the air quality in some highly-possible future scenarios.
Keywords: atmospheric pollution, simulation, models, OSPM.

1 Introduction

Air pollution is one of the most severe problems in urban areas. In recent years, the Thermophysical Properties Laboratory of Chemical Engineering Department in Aristotle University has focused on the study of the atmospheric pollution of the historical centre of Thessaloniki. In order to estimate the air pollution, solely due to traffic, the well-known OSPM model [1], is employed. This model has been widely used in the past [2] and validated for similar cases [3, 4].

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1.1 Overview

OSPM is developed for practical applications and especially for the estimation of pollution due to traffic in street canyons. The model employs a simplified parameterization for the conditions in a street canyon, influenced by the wind flow and the pollutants dispersion. Pollutants' concentrations are calculated by using a combination of a Gauss model (for the direct contribution) and a box model (for the recirculation in the street canyon). To estimate vehicles' technology distribution in future years, the model TRENDS [5] is employed.

Unfortunately the application of models such as OSPM for a certain period of time (e.g. a year), requires a large amount of input data, which in most cases, is not available. For this reason, the authors aim to examine OSPM's application in the absence of sufficient data and to propose specific actions to elaborate this significant drawback. The work presented here, consists of three main parts: i) the enumeration of the input data and their sources, and the identification of the area of interest, ii) a specific evaluation of OSPM and iii) the estimation of some atmospheric pollutants for two future scenarios (table 1).

2 Input data

For the calculations, the following input data are required: i) streets' geometrical configuration, ii) meteorological data (temperature, wind speed and direction), iii) background concentration of each pollutant and iv) pollutants emissions. The latest version of OSPM (WinOSPM/2003) contains a fully integrated emission module that uses the traffic characteristics, such as the technology of the vehicle fleet, a mean speed and vehicles' number, to calculate hourly emissions due to traffic. Table 2 describes the necessary input data and their sources.

Table 1: Description of elaborated scenarios.

No	Description
1	June and February of 2004
2	June and February of 2010 according to TRENDS' estimation
3	June and February of 2010 according to authors' raw estimation

Table 2: Input data sources.

Data	Source
Streets' geometrical configuration	City Traffic Study [6, 7]
Meteorological data	Station SV2BBO [8]
Background concentration	AirBase EIONET [9] (Stations of Panorama & Neochorouda)
Pollutants emissions	COPERT III [10]
Traffic load	Public Works Office [11]
Number of vehicles per technology	TRENDS [5]

Figure 1: Area map.

2.1 Area of interest

The city of Thessaloniki is located in the northern part of Greece, on the coast and it has almost 1.5 million citizens. It is considered to be one of the most polluted cities regarding the airborne particles (e.g. PM10). Figure 1 shows the area of interest, which is the historical centre of the city.

In figure 1, the highlighted streets are those incorporated into the main model (which will not be shown here), while the numbered ones are the streets in which this work is focused. The area in the grey circle represents the area where measured data are available.

2.2 Missing data

Although in the past OSPM has often been employed [2] and was shown to perform very well, the case of Thessaloniki is a difficult one as a lot of the required data are not available or their accuracy is questionable. In the following sections problems encountered in each dataset will be presented together with the authors' suggestions for ways to overpass them.

2.2.1 Streets' geometrical configuration

The streets' geometrical configuration refers to the street's width, length and the height of the buildings at its side. The width was obtained from literature [6,7], while the length was measured by the authors. The height of the buildings however, can only be estimated as an average, as it differs from building to building.

2.2.2 Meteorological data

There is an abundance of meteorological data (Station SV2BBO [8]). There are in general, available on an hourly base and the station is positioned near to the area of interest. These data are collected by an amateur enthusiast, and there is a lack for some time periods.

2.2.3 Background concentrations

The background concentration strongly affects the calculated total concentration. This is also not available for the whole year and for some specific pollutants, a whole year is even missing. In those cases where the background concentration is not available, comparisons or future scenarios can only refer to contributions to air pollution due to traffic.

2.2.4 Traffic load and vehicles technology

Traffic load for every street is unfortunately, available only for one or two days for each year. This means that, estimating air quality for a whole month or year will be based only on a day's measurements. However, it is noticed that traffic load does not vary much even between consecutive years, which indicates that a limit has been reached. On the other hand, it is also well known that traffic load varies enough between week days, and this is the first drawback for such projects. Table 3 describes the number of vehicles per scenario (defined in table 1), fuel and EURO technology.

Table 3: Number in thousands of vehicles per scenario, fuel and EURO technology (TRENDS [5]).

	Fuel								
	Gasoline			Diesel			LPG		
	EURO Technology								
	No	I-III	≥ IV	No	I-III	≥ IV	No	I-III	≥ IV
Passenger Vehicles									
1	1,156	2,356	-	3	647	-	3.5	4.5	-
2	726	2,525	1,067	-	-	-	2.6	4.9	2.4
3	568	1,898	802	285	539	268	-	-	-
Trucks									
1	544.8	288	-	12.9	79.2	-	-	-	-
2-3	372.2	360	155.9	86.3	97.2	10	-	-	-
Busses									
1	-	-	-	7.5	6.7	0	-	-	-
2-3	-	-	-	5.5	7.7	2.3	-	-	-

Vehicles' technology distribution is well established for the whole country and it is easy to project the same distribution to the second largest city. But the problem is that this distribution might vary between streets and this variation can affect the results. Furthermore, vehicles' average hourly speed is based on a simple assumption that it will vary according to the total traffic load of each street. The lowest and the highest speed were selected and then speeds distribution was set to follow the distribution of the traffic load.

3 Comparison and evaluation

In order to perform the comparison between the OSPM output concentration and the measured one [9], the following ought to be taken into consideration

- average building heights are assumed,
- meteorological data are available more or less (so this is not a problem)
- as the background concentration is only available for NO_2, and also measurements for NO_2 exist, this is the pollutant that the comparison will be based upon (measurements for PM10 are not adequate and data on O_3 were not considered as it is not clear whether OSPM takes into account O_3 photochemical effects, while it does take them for NO_2 [12]),
- although the number and technology of vehicles are available, the traffic load is only available for a single day (May 5th, 2004). Hence, all comparisons will be restricted thereafter for this particular day.

3.1 Results

All results refer to the area of interest (figure 1). The concentration of each neighbouring street is calculated for every hour and shown in figure 2, together with their hourly average, and the measured values. The background concentrations as well as the EU limit for 2004 (given by OSPM) are also shown. As it can be seen from figure 2, the average hourly concentration agrees excellently with the values measured in that area. To our opinion this confirms the validity of our methodology and hence this methodology can be applied to the estimation of other pollutants' concentrations where no measurements or other parameters exist.

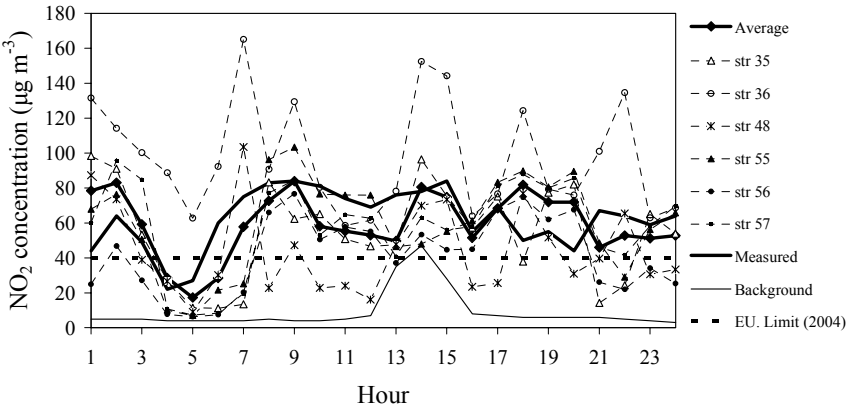

Figure 2: NO_2 concentration (μg m^{-3}) by hour for neighbouring streets.

As an example of this statement, in figure 3, we show the equivalent concentrations for PM10. It is of great interest, that although the concentrations of PM10 are quite high (and surely much higher than the EU 2004 Limit), there

are almost no measurements of PM10. Also it is interested to note that even the background concentration of PM10, which is clearly attributed to the industrial area around the city, is much higher than the EU 2004 Limit. These two points, as well as the high NO_2 concentrations, should be of prime importance to the authorities in Thessaloniki.

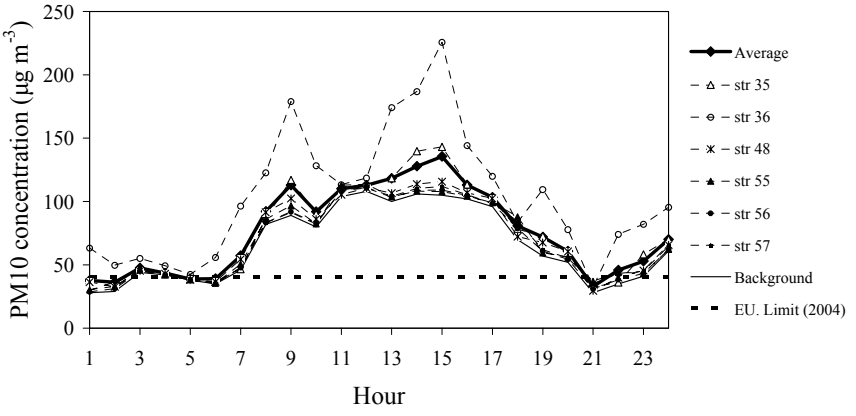

Figure 3: PM10 concentration (μg m^{-3}) by hour for neighbouring streets.

3.2 Sensitivity analysis

In the previous section, by applying our methodology for a particular day, it was shown that the values calculated by OSPM agreed excellently with the measured values. To conclude this analysis, it will be of interest to establish a sensitivity analysis for the five main parameters entering OSPM. Figure 4 illustrates as an example, the influence of these parameters to the calculated concentrations deviating from those for a base case (2004, only passenger cars, street no 55), for five pollutants. It can be seen that the most sensitive parameter, in this case is the width of the street canyon followed by the short vehicle velocity. It can also be seen that the Cold Start parameter has almost no effect.

4 Future scenarios

A complementary aim of the present work is to estimate the future state of air quality in Thessaloniki. Two future scenarios were chosen (see table 1) both for 2010. Meteorological conditions, streets' geometrical configuration and background concentrations were considered identical to the values of 2004. Traffic load and vehicles technology (table 3) for 2010 and the whole country were calculated by TRENDS [5]. To estimate the hourly traffic load per street for Thessaloniki, it was assumed that vehicles distribution per hour and street remains the same as in 2004.

However, the forecasted vehicles' technology distribution predicted for 2010 by TRENDS, assumes that LPG vehicles will replace almost all passenger diesel vehicles and does not take into consideration the fact that the market of diesel vehicles in Greece will be released. For this reason an alternative scenario, scenario 3, is proposed, which is based on a common belief, that 1/4 of passenger vehicles in 2010 will use diesel as a fuel, and not LPG.

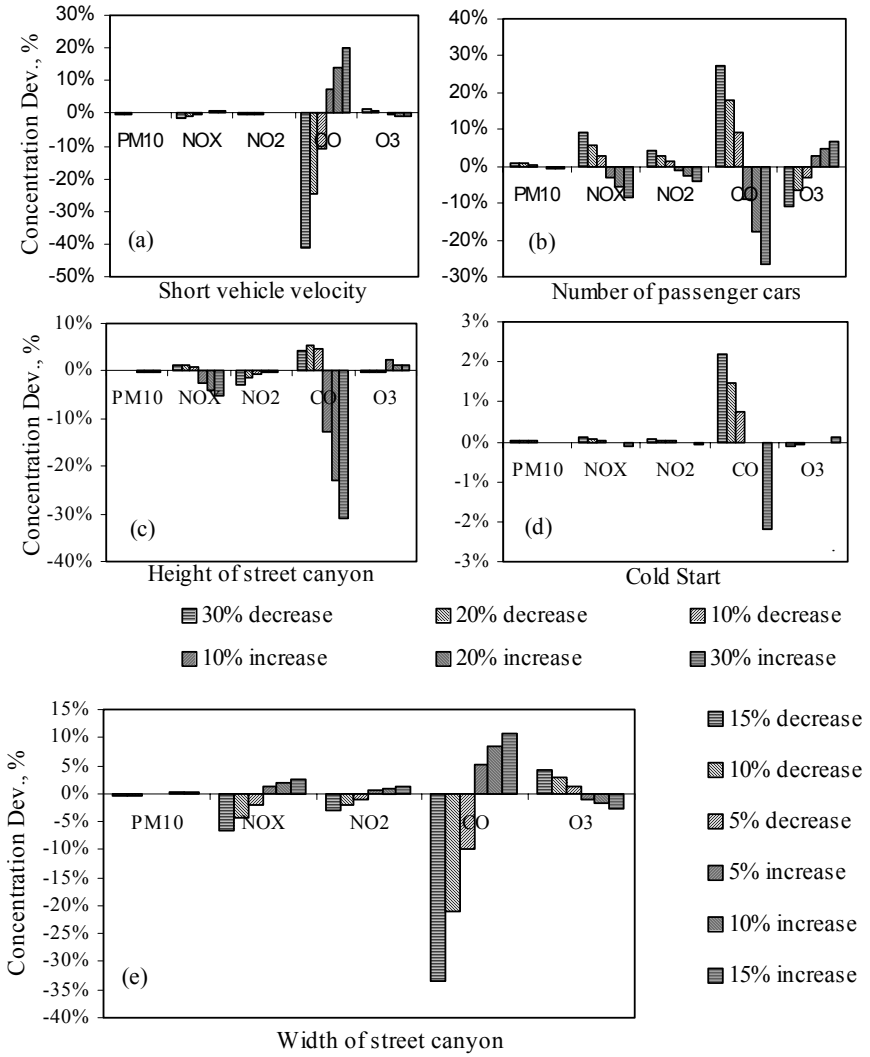

Figure 4: Sensitivity analysis for five important input parameters, for five pollutants.

4.1 Results and discussion

Figures 5-7, illustrate the concentration deviations, for pollutants NO_2, PM10 and CO for scenarios 2 and 3, from scenario 1. Concentrations shown are indicative for the month of February.

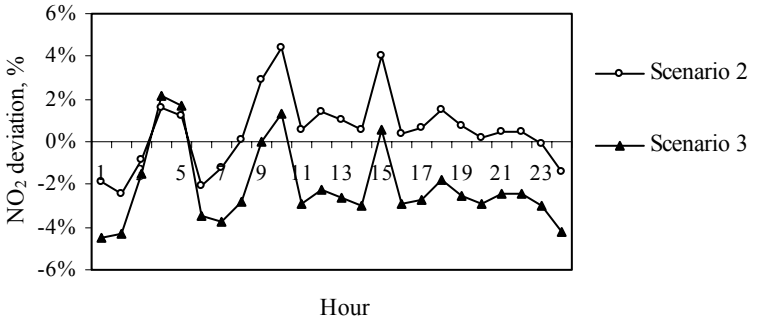

Figure 5: NO_2 hourly concentration deviations (%) from scenario 1.

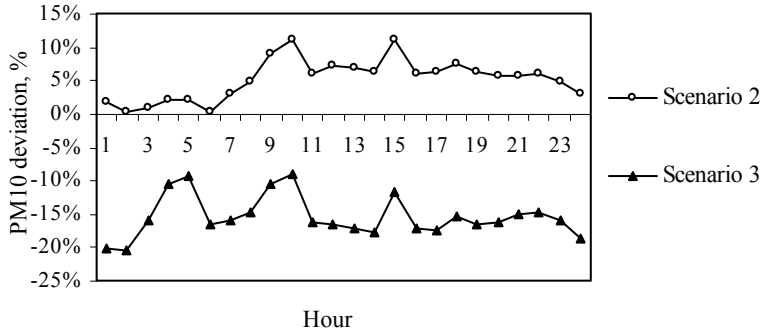

Figure 6: PM10 hourly concentration deviations (%) from scenario 1.

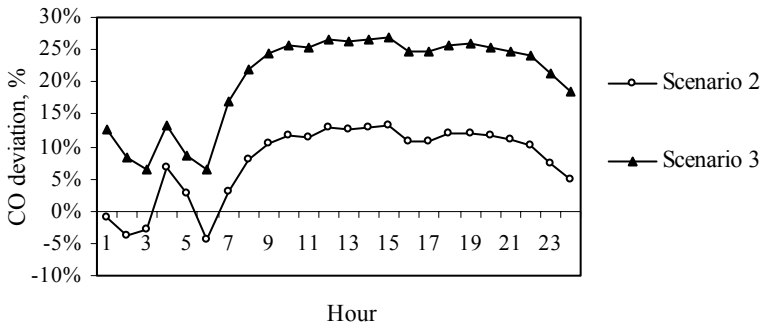

Figure 7: CO hourly concentration deviations (%) from scenario 1.

NO_2 levels of concentration show only a small deviation from scenario 1 (2004), which is expected as: i) gasoline vehicles are the main source of NO_2 [12], ii) number of gasoline vehicles varies 25% between scenario 2 and 3, and iii) as the number of vehicles increases their anti-pollution technology is bound to develop.

On the other hand, PM10 concentration increases significantly between from scenario 2 to 3, mainly because of the increase of diesel cars. This increase in the number of diesel cars (which means decrease in gasoline vehicles) however, will result in a decrease in the levels of CO concentration, which is seen in Figure 7.

5 Conclusions

In this work, a methodology was put forward in order to employ OSPM in cases where insufficient data were available. As an example, the city of Thessaloniki was considered. To complete the successful application of the methodology, as confirmed by comparison with measurements, a sensitivity analysis was proposed. Finally, OSPM was employed to predict air-quality in Thessaloniki in 2010. A probable increase in the number of diesel vehicles will result, as expected, to an increase in the concentration of PM10 and a decrease in the concentration of CO.

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Barriers and opportunities to successful local air quality management consultation in England

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Abstract

England now has some 10 years experience of the Local Air Quality Management (LAQM) process where local authorities are required to consult on their air quality findings with stakeholders and the public. The statutory basis for consultation is provided by the Environment Act 1995, part IV; the Act and subsequence Policy Guidance identify a range of statutory and non statutory consultees, including the public where it is appropriate that their views are taken into account in the local authority's decisions about LAQM. This paper will present the outcomes of a 2 year Economic and Social Research Council funded programme addressing how local authorities in England have discharged their air quality duties and responsibilities. Evidence from a questionnaire survey and case studies is presented. Data suggest that although local authorities genuinely attempt to engage with all stakeholders, current consultation processes are not working as well as they could. This suggests a re-think on the form and function of LAQM consultation processes is required. Barriers for and opportunities to effective consultation will be considered and the paper will conclude with a set of parameters that define an integrated LAQM consultation process.
Keywords: consultation, air quality management, England.

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1 Introduction

1.1 Legislative context

The Environment Act 1995, part IV, requires local authorities to review and assess air quality in their area of jurisdiction and determine locations where concentrations of health-based air quality objectives are likely to be exceeded. The Act has also placed an obligation on local authorities to consult with local stakeholders as part of their local air quality management (LAQM) process. The Act [1] and subsequence Policy Guidance [2] identify a range of statutory and non-statutory consultees, including the public, where their views should be taken into account in the local authority's LAQM decision-making process.

The Environment Act 1995 provides the minimum legal requirements for consultation and Schedule 11 of the Act states that:

"A local authority in carrying out its functions in relation to a) any air quality review, b) any assessment under section 82 or 84 of this Act, or c) the preparation of an action plan or any revision of an action plan shall consult such other persons as fall within sub-paragraph (2)." Appendix 1 provides a list of statutory consultees as required by the 1995 Act.

The LAQM Policy Guidance [2] recommends wider involvement through the inclusion of other groups, such as residents and local business, in the policy development process. Including non-expert views and opinions reflects a growing trend in environmental decision-making that acknowledges the need for local networks of communities to be involved in the process of LAQM. The guidance also provides suggestions on how local authorities should consult and liaise with others. It is stated clearly that within a full round of air quality review and assessment, there are a number of opportunities for local authorities to consult. Figure 1 illustrates the Government's recommendations on the approach to consultation that should be adopted in the second round of air quality review and assessment. However, the extent of the consultation is at local authorities' discretion. Although there is no need for a full public consultation at each step of the review and assessment process, local authorities will still wish to make their air quality assessments available to the public [2].

1.2 Local Air Quality Management Consultation

Previous research on communication initiatives relating to air quality indicates that participants struggled with the scientific concepts and modelling procedures presented. However, given effective access to information, communities are capable of incorporating and integrating a broad range of technical and social factors involved in making viable decisions about local air quality [3]. These findings are in line with earlier study suggesting that the public make sense of air pollution information in relation to their personal experience, put into 'real-world' context [4]. Previous research by Beattie *et al* [5] suggests that a different range of consultation strategies: one-way (e.g. provision of leaflets in libraries), two-way (e.g. questionnaire survey), and to a limited extent, participative (e.g.

public meetings and citizen's juries) were used to inform and consult stakeholders about the process of LAQM. General advice on consultation for LAQM is provided by the National Society for Clean Air and Environmental Protection (NSCA) [6]. Details about the process of LAQM are provided by Longhurst *et al* [7].

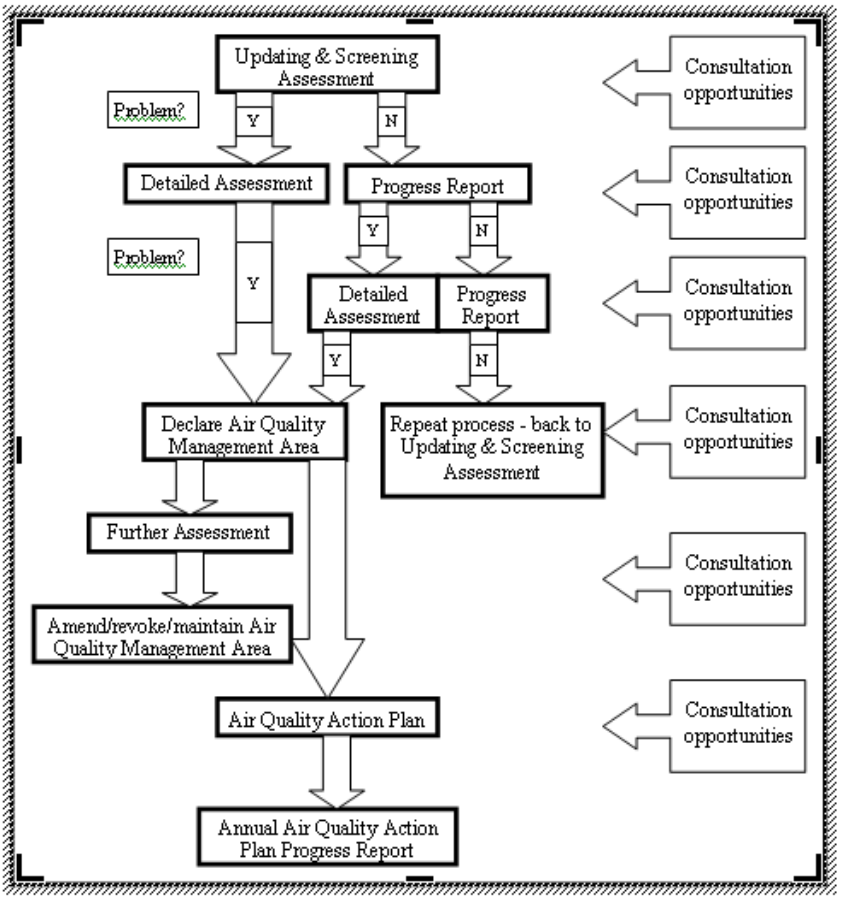

Figure 1: Local air quality management – opportunities for consultation.

This paper will present the outcomes of a 2 year Economic and Social Research Council funded programme addressing how local authorities in England have discharged their air quality duties and responsibilities. The aims of this research were to investigate the nature, scope and effectiveness of local authority's approaches in LAQM consultation and to develop a conceptual model of better practice in LAQM consultation. The latter is discussed elsewhere [8]. This paper will conclude with guidance on steps to better practice to LAQM

consultation, which is designed for local authorities to engage with stakeholders and local communities in meaningful and effective dialogue on air quality issues.

2 Methods

The data presented here are drawn from questionnaire survey and case study research. A semi-structured questionnaire was designed to identify the actual stakeholders consulted by local authorities on air quality related issues, the aspects of review and assessment consulted upon including how stakeholders' views affected decision-making process, and different methods of consultation used. A pilot survey was sent out to all local authorities in Scotland and Northern Ireland. Following minor amendments, a final questionnaire survey was sent by mail to all local authorities in England (n=353), primarily directed at environmental health professionals responsible for implementing the LAQM regime.

Following a rigorous case study selection criteria [9] 11 local authorities were chosen for case study research. Case study authorities were selected to provide a geographical spread throughout England, to represent differing administrative type (a district, London, Metropolitan or unitary authority), and differing local air quality challenges (with or without Air Quality Management Area). Semi-structured interviews were used as the primary data source, supplemented with the government archive on air quality, local authority reports and other documentation related to air quality work in the case study locality, as well as their response to the postal questionnaire.

3 Research findings

The questionnaire survey provided a broad picture of LAQM consultation practice in English local authorities whilst case studies covered a more limited number of authorities in more depth. These data sources were used to investigate the nature, scope and effectiveness of local air quality management consultation approaches. Responses to the postal questionnaire were received from 150 authorities (a response rate of 42%).

Schedule 11 of the 1995 Act requires local authorities to carry out consultation with statutory consultees (see Appendix 1) and subsequent policy guidance advises consultation with the public, local businesses and other stakeholders as appropriate. Given this framework, nearly all survey participants (94%) stated that they had undertaken consultation although surprisingly the remainder never undertook any consultation on the LAQM process.

3.1 Local Air Quality Management Consultation practice: stakeholders and their impacts in the decision-making process

Survey participants were asked to identify internal departments within their local authority and external bodies consulted during the LAQM process. LAQM consultation was carried out primarily by the environmental health department,

either alone (57%) or in partnership with other departments (43%). A vast majority of internal consultation undertaken to incorporate other departments' views and opinions on air quality management issues was with land-use planners (90%), followed by consultation with transport planners (77%) and Elected Members (74%). Department for Environment, Food and Rural Affairs (Defra) was viewed as the most significant statutory stakeholder although 10% of participants considered their submission of air quality review and assessment reports to Defra as routine reporting in order to get a seal of approval rather than as consultation. Further results from the survey revealed that residents were considered to be as important as the County Council in LAQM consultation (score 2.1; with 1 = very important to 5 = not important) whilst neighbouring authorities (score 2.2) were slightly more important than the Environment Agency and Highways Agency (both score 2.3).

Subsequent case studies showed that although most authorities attempted to consult both statutory and non-statutory stakeholders on LAQM issues, there existed a distinct emphasis towards engagement with formal, institutional, and expert statutory consultees. Evidence from case studies suggested a number of reasons for this: a) local authorities tended to *"feel at ease with fellow professionals"*, b) were concerned that *"people do not seem to get [understand] the numbers from monitoring and modelling"*, and c) struggled to elicit responses from non-statutory consultees as *"they do not show any real interest"*. In other words, even though residents were considered as an important stakeholder in the LAQM consultation process, local authorities may have tended to limit their engagement with non-experts, and sought to expand dialogue with a range of expert statutory institutions who were perceived to have a better understanding of, and interest in the underlying science and policy issues.

In order to undertake meaningful consultation, it is important to ensure that all consultees views are considered and incorporated into the decision-making process. In the survey, a question was asked to find out whether consultation actually influences local authority's decision, and if it does, at which stage of the LAQM process. Table 1 shows the extent to which stakeholder views have an impact on different stages of LAQM. The most significant impact was on choosing measures to be put forward in Air Quality Action Plans.

This opinion is confirmed by case study authorities although they also experienced difficulties in integrating the views of non-statutory consultees, which include the public, in the decision-making process, in particular how to weigh, report, and embed responses in Air Quality Action Plans. This is probably because local authorities tended to feel more at ease with statutory consultees, and feel more able to include their responses. Case study research also found that local authorities experienced difficulties in drawing down sufficient funding to implement Action Plans fully. As Action Plans are one area where non-statutory stakeholders were most likely to be involved, there is a view that consultation unfairly raises community's expectations.

Table 1: Local authority views on the impact of stakeholders' views on LAQM decision-making.

Decision-making process	*Score**
Decisions to proceed to Detailed Assessment	3.7
Conclusions of Updating & Screening Assessment	3.6
Conclusions of Detailed Assessment	3.6
Revocation or amendment of Air Quality Management Area	3.4
Decision to declare Air Quality Management Area	3.1
Air Quality Management Area boundaries	3.1
Local Air Quality Strategies	3.0
Measures put forward in Air Quality Action Plans	2.5

*1 = very significant and 5 = insignificant

3.2 Successful Local Air Quality Management consultation

While UK policy emphasises the importance of local authority involvement and engagement with a broad range of statutory and non-statutory community stakeholders, the reality of such engagement is often more complex and uncertain.

Local authorities were asked to judge whether LAQM consultation has been undertaken successfully. Only 40% of survey participants considered their consultation to be successful whilst nearly 44% were unsure of the outcomes. Reasons why consultation might not be considered successful included: limited responses from consultees, particularly in relation to consultation with the public, lack of interest from and interactions with other departments in the local authority and relevant government bodies, lack of resources and limited experience in consultation. In local authorities' views, the process of consultation can be improved by having more resources i.e. time and funding, sharing best practice, having more training, and making better use of websites. A lack of expertise on undertaking LAQM consultation was also identified. Most questionnaire participants stated that they had never received any formal training. This finding corresponds with case study evidence where local authorities stated lack of experience and expertise in consultation. This is perhaps unsurprising given the range of roles and duties that environmental health departments are expected to perform. In the context of this gap of expertise, the research team have developed a practical guidance document entitled "Steps to Better Practice: Guidance for local authorities on LAQM consultation" [10] (available to download at www.uwe.ac.uk/aqm/esrc).

One case study authority considered to execute "better LAQM consultation practice" [8] demonstrates that effective LAQM consultation can be done. The authority managed to join together statutory and non-stakeholders in carrying out LAQM consultation. These range of stakeholders included officers from environmental health, transport, and planning departments in the local authority, local residents and businesses. More importantly, they were able to maintain active engagement initiatives throughout the years using a pollution

measurement partnership programme. Consultation works well when non-statutory stakeholders (informal networks) are empowered to interact with statutory stakeholders (formal networks). This interaction is best enabled by local community champions, advocates of local authorities and politicians. The consultation process also needs to be adequately resourced and carried out over a reasonably extended time-frame. It is also critical to decide the point at which consultation takes place.

4 Conclusions

Evidence from questionnaire and case studies suggest that there is no simple solution to successful LAQM consultation. Although local authorities genuinely attempt to engage with all stakeholders, current consultation practices are not working as well as they could. This may imply a re-think on the form and function of LAQM consultation processes. This paper argues that consultation is a key element in LAQM process and meaningful consultation can win public and political supports on what might be difficult and challenging actions to improve air quality. The strategic co-ordination of a range of engagement initiatives contributed to a more effective LAQM consultation process. Early and up-stream engagement practices within the consultation process build local community participation and allow for a clearer broad-based stakeholder constituency to thrive and influence the process of LAQM.

Based on the research findings, a set of parameters have been set to define an integrated LAQM consultation process. The parameters are as follows:

- stakeholder engagement should be early and upstream, and have the capacity to effect real change via a clear association with the LAQM decision-making process;
- stakeholders should be well-informed, be aware of the opportunities to participate and, optimally, be able to engage over an extended time period;
- local authorities and their stakeholders commitment to be involved in the process are best enabled via experienced and effective LAQM advocates of local champions (within the community, local authority, and amongst local politicians);
- consultation works well when local authorities and their communities are able to access adequate resources levered by relevant funding streams;
- trust and capacity building in the process can be built through co-work exercises, for example via pollution measurement partnerships, public health initiatives or relevant environmental and transport projects.

Appendix

(2) Those persons are –
  (a) the Secretary of State;
  (b) the appropriate new Agency;

(c) in England and Wales, the highway authority for any highway in the area to which the review or, as the case may be, the action plan or revision relates;
(d) every local authority whose area is contiguous to the authority's area;
(e) any county council in England whose area consists of or includes the whole or any part of the authority's area;
(f) any National Park authority for a National Park whose area consists of or includes the whole or any part of the authority's area;
(g) such public authorities exercising functions in, or in the vicinity of, the authority's area as the authority may consider appropriate;
(h) such bodies appearing to the authority to be representative of persons with business interests in the area to which the review or action plan in question relates as the authority may consider appropriate;
(i) such other bodies or persons as the authority considers appropriate.

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Www.airqualitynow.eu, a common website and air quality indices to compare cities across Europe

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Abstract

Air quality is a public concern. This is partly due to the "right to know" principle embodied in European legislation. Despite this common legislation, the way air quality is being interpreted and communicated differs considerably. For specialists raw monitoring data for Europe are available but these are not usable by the general public. Easy to understand and internationally comparable air quality information from one city to another is scarce. The CITEAIR project facilitates the comparison of urban air quality in near real-time by introducing two products: common air quality indices (hourly, daily and annual), implemented on a common website www.airqualitynow.eu. This paper describes these indices and presents their application on the common website. The indices and the website both aim at presenting the air quality of the participating cities in a comparable way. The website is designed to receive and display data from each city wanting to join. The main part is dedicated to compare the cities index values using different time scales (hourly, daily or annual) and for two types of exposure thanks to a background and a traffic index. In addition, space is offered to cities for presenting themselves according to a common template, providing background information on their specific air pollution situation and associated reduction measures. Participating is easy: cities upload their data through ftp and the indices calculations are automatically made. The website provides a dynamic picture of the air quality and is updated each hour enticing viewers to make repeated visits. However, participation with only a daily update or with yearly data is feasible as well. The indices and the website do not aim to replace more targeted local information. Their value added is to provide, for the first time, a European and comparable picture of the air quality in near real-time easily accessible through a common platform and presentation of the results.
Keywords: air quality index, public information, website, European platform.

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1 Introduction

The Framework directive and associated daughter directives on air quality in the European Union not only force member states to monitor and report on their air quality but also to actively inform the public on the status of the ambient air quality. The Aarhus convention, ratified by the EU in 2005, further enforces the concept that citizens have the right to be informed on the environmental conditions they live and work in. Over the past years a good number of cities and countries have started to display monitored or modelled air quality data on the internet. For most of the monitoring organisations, the internet is the easiest way to meet the dissemination of information requirements of the European (and/or national) legislation. The fact that so much air quality information is available on the internet makes it tempting to compare different cities in different countries. This proves particularly difficult. Apart from technical websites such as the European Environmental Agency's ozone website [1] and Airbase [2] there are no possibilities to compare cities/countries side by side. Even if one surfs from one site to the other, comparison is not easy: air quality is presented in different ways using different interpretation criteria and a different typology of stations, which is usually not clearly explained.

The most widespread way to interpret air quality on websites is the use of an index ranging from good to bad to make the detailed measurements in micrograms more understandable for the general public. A review of existing websites and the associated air quality indices shows that the way air quality is interpreted differs considerably across the world. More surprisingly, even amongst the EU member states who share common legislation, the indices used do vary. There are a number of reasons to explain these differences. Some of them are historical, others conceptual: the index existed before the EU regulations came into force or the index is based on health and exposure criteria, e.g. the UK index [3]. The fact that air quality problems (sources, meteorological conditions, etc.) tend to differ is also one of the reasons. The indices tend to be calibrated to the local situation, for example, to make sure that there is some variation in the index from day to day (to entice repeated visits) and that the typical range of pollutant conditions occurring locally is being covered.

To facilitate the international comparison of near real time air quality the CITEAIR project [4] (co-funded by INTERREG IIIC) has developed a common operational website www.airqualitynow.eu where cities can display their air quality information side by side. The project aims at making air quality comparable across Europe and www.airqualitynow.eu is already open for any city to join. The common website relies on common air quality indices (hourly, daily and annual). The comparison possibilities offered to the public are on an hourly, daily and yearly basis and the indices were developed keeping in mind that the general public is the end user. This paper presents the CITEAIR common website and its set of indices. It explains how they have been elaborated through collaboration between the partner cities (Leicester, Paris, Prague, Rome and Rotterdam) and is now open to any city willing to participate.

2 International comparison of cities air quality on the internet

2.1 Difficulties in comparing the European cities air quality

CITEAIR provides a common index and makes a difference between background and traffic stations. The potential of having a common index on the same website will be apparent from the following example in which we try to compare air quality at a given day in four cities. The indices are described in Table 1. Three out of four cities have an index, two indices range from 1 to 10, the other from 1 to 200. Two cities have 10 classes, one has 5, one has 4. Two describe air quality in terms of good and bad, one in terms of health and the fourth in terms of pollution levels. The class boundaries are very different. In addition, whereas most websites have a page explaining how the index is calculated, other methodological aspects are generally not explained. Does the index represent measurements at background stations, traffic stations, a mixture?

Table 1: Indices used on the internet in Paris, Leicester, Rome and Rotterdam (situation in 2005)

ATMO Paris	ozone-1h	PM10-24h	NO2-1h	index	**UK**	ozone-8h	PM10-24h	NO2-1h	index
Very good	29	9	29	1	low	32	21	95	1
	54	19	54	2		66	42	190	2
good	79	29	84	3		99	64	286	3
	104	39	109	4	moderate	126	74	381	4
average	129	49	134	5		152	86	477	5
mediocre	149	64	164	6		179	96	572	6
	179	79	199	7	high	239	107	635	7
poor	209	99	274	8		299	118	700	8
	239	124	399	9		359	129	763	9
Very poor	>=240	>=125	>=400	10	very high	>=360	>=130	>=764	10

Rome	ozone-1h	PM10-24h	NO2-1h	index	**Rotterdam***	ozone-1h	PM10-24h	NO2-1h	index
good	90	100	100	50	good		20	100	-
moderate	135	150	150	75	moderate	180	40	200	-
mediocre	180	200	200	100	bad	240	60	400	-
unhealthy	360	400	400	200	very bad	>240	>60	>400	-
very unhealthy	> 360	> 400	> 400	>200					

* Ozone classification from the national smog pages, other classes from a local traffic website.

If someone would like to compare these four cities at a given moment he or she would not only have to visit four websites but also be faced with four completely different presentations, qualifications and languages. Apart form the fact that the bands differ from one country/city/area to the other, the data behind the index also differ. This is hard for a specialist and almost impossible for the general public. The CITEAIR initiative comes from this situation.

2.2 Comparing European cities thanks to a common website

The CITEAIR common website www.airqualitynow.eu has been launched in March 2006. www.airqualitynow.eu is meant to be an interesting complement to the cities own websites. The website and the corresponding indices are not launched to replace existing websites or indices. Their value added is to provide for the first time a European and comparable picture of the air quality at first glance, up to date and understandable by anybody for:

- three time scales (on a hourly, daily and an annual basis),
- and two types of public exposure to air pollution (background and traffic conditions).

In addition, for those cities that are not yet on the internet, and/or do not currently use an index, "air quality now" and its indices could be their primary platform to easily provide information to the public and the local authorities. A space is also offered to cities for presenting themselves according to a common template, providing background information on their specific air pollution situation and associated reduction measures.

The website is operational with 16 cities feeding their data (see Figure 1). Some developments are still ongoing to improve its design and ergonomics and other cities are invited to join and upload their data as well. The process to join has been made easy. Based on the data sent by the cities through an agreed ftp format, the indices calculations are automatically done inside www.airqualitynow.eu. The full procedure is detailed on the "join us" page. However, not every city has its own monitoring network or both traffic and background stations, and not everyone is able to deliver data in near real time. If cities want to participate in only one of the indices, can only deliver data on a daily basis, or even only present year average data, they can still join the website. Different sections of the website provide a platform to compare different data (year average, daily, hourly). Participation is therefore not limited to those with their own automated monitoring network.

Www.airqualitynow.eu does not aim to replace more targeted existing local information. This would be an unrealistic ambition as in many cities the public has got used to the local, tailor-made index. The proposed common indices are, by the nature of the fact that they are common to a wide area, a non-specific compromise. CITEAIR envisages that there is room for two sources of air quality information on the internet: a local website, in the national language with a dedicated presentation (often using a well established and known local index); and a common website aimed at comparing – in near real time – the air quality in your own city to the air quality in other European cities.

Figure 1: Home page of the CITEAIR common web site www.airqualitynow.eu presenting the comparison of air quality in European cities through common indices.

3 International comparison of cities thanks to common air quality indices

3.1 Review of air quality indices

There are a number of different ways to interpret air quality in near real time. The most common way to do so is the use of an index, generally based on a number of sub-indices for individual pollutants. Air quality indices aim to translate the chemical characteristics of a quite complex mixture of pollutants in the air into one single figure. From a scientific point of view this is obviously a gross generalisation but for communication purposes it is considered an essential simplification. An index is also always a compromise between several objectives and potentially occurring situations. The trade-offs in developing the common indices were made having in mind that they should be applicable over a wide range of conditions and interesting to the public.

There is a wealth of indices and countries that share the same legislation, or sometimes even areas/cities within the same country, have different

indices [5, 6]. Some of the differences can be explained by the local differences in the nature of the air quality problems. Some other differences are due to fundamentally different approaches. For example, the UK and US-EPA indices [7] are strongly related to perceivable health effects. The bands in the index are explained in health terms. This implies that the index covers a very wide range of concentrations and that the observed concentrations are very often in the "good" or "moderate" end of the scale. Air quality in Europe, fortunately, is rarely poor enough to cause acute health effects so any index based on health impacts tends to trail at the lower end of the scale for most of the time.

Other indices take a different approach. For example the ATMO index, based on a national regulation concerning all French cities larger than 100 000 inhabitants [8] has bands that are somehow linked to values that are also used in the current EU directives. The alert thresholds in the directives tend to define the higher end of the scale. In these cases the top end of the index scale ends somewhere in the middle of the health effect based scales. For example the worst end (very poor) of the NO_2-index in France corresponds to 400 μg/m3. In the UK this is in the lower end of the "moderate" band and in the US it is even considered too low to calculate an index value.

Communication-wise the health-based indices have both a clear advantage and a disadvantage. The advantage is that the index value displayed at the website is easy to interpret: it does or does not cause health effects. The disadvantage is that the index is almost always indicating that air quality is good and pollution is low whereas the limit values for long-term exposure are often exceeded. This leads to an apparent paradox: a citizen regularly checking the local air quality website will always get the message that the air quality is good whereas at the end of the year local government puts out a report that he or she is living in a hotspot area for which an action plan is required. This is the paradox between short- and long-term air quality criteria. The criteria for short-term exposure are often met except for episodes, like for example in the summer of 2003. The criteria for long-term exposure are often not met in Europe's urban areas. The ATMO-type of indices provides some differentiation at the lower end of the scale to assure that the air quality is not always "good". However in this case it is very difficult to attach some kind of health interpretation to the index.

The long-term vs. short-term paradox typically occurs on the internet. In an annual report the focus is on long-term air pollution and in the teletext pages dedicated to smog warnings the focus and interpretation is based on short-term health effects. However, internet presentations often serve multiple roles: informing the public, but also making the public aware of air quality issues. In this case the paradox is difficult to resolve: highly variable hourly (or daily) data is being presented to assure an attractive and frequently changing presentation that encourages repeated visits. On the other hand, the most challenging limit values appear to be the criteria for the year average so interpreting commonly occurring hourly values in terms of good or bad is fairly arbitrarily. They are not bad from the short-term exposure point of view but might be bad from the long-term exposure point of view. This explains the need for an annual index as well.

3.2 A common daily and hourly index (CAQI)

As already explained, comparing air quality in different cities is a tricky issue. Is the air quality being determined in the same way (this mainly applies to particulate matter) and at comparable locations? This is not an issue that the CITEAIR project and its indices can solve. Its common website will take for granted whatever a city supplies as input in either category. As a first step to improve comparability, the indices will be reported both for roadside and city background locations. This is considered an important improvement over city averages: some monitoring networks are designed to monitor or spot areas of poor air quality (with possibly a high number of roadside stations) whereas others are aimed at providing an average city picture.

The Common Air Quality Index (CAQI) is used both for a daily index and for an hourly index. In the website the daily index will be shown for the past day (D-1). For the current day, the hourly index will be available, to be updated every hour. A daily index for today would need forecasting or 'nowcasting' a facility that is not available in each city with a monitoring network, hence the option of an hourly index. The hourly index is also a reasonably dynamic parameter, enticing repeated visits to a website.

The CAQI is calculated according the grid in Table 2, by linear interpolation between the class borders. The final index is the highest value of the sub-indices for each component. As can be seen there are two CAQI-s: one for traffic monitoring sites and one for city background sites. The traffic index comprises NO_2 and PM_{10}, with CO as an auxiliary component. The background index obligatory comprises NO_2, PM_{10} and O_3, with CO and SO_2 as auxiliary components. In most cities the auxiliary components will rarely determine the index (that is why they are auxiliary) but in a city with industrial pollution or a seaport SO_2 might occasionally play a role. Benzene is considered a long-term exposure issue. The number of cities with online monitoring benzene is limited and it is therefore not included in the short-term indices.

The choice of the classes in the CAQI is inspired by the EU legislation and based on a compromise between the participating cities. The dividing line between medium and high is often linked mainly to the values mentioned in the directives: alert thresholds (SO_2, NO_2, O_3) or air quality objectives when available on a daily basis (CO and PM_{10}). Class borders were regularly spaced for the main components. PM10 is an exception. To avoid that the CAQI is completely dominated by PM_{10} the value of 50 $\mu g/m^3$ as a daily average was positioned as the bordering line between low and medium. For the setting of the CO and SO_2 borders additional inspiration was sought from the DAPPS index [9] which aims to define the component sub-indices based on the relative risks attributed to each component.

PM_{10} poses a particular problem. Many networks only report 24-hour (moving) average data. This different averaging time implies that their concentration readings are always lower than those for the networks reporting true hourly values. To resolve this inconsistency 24-hour averages are divided by 0.63 the average ratio between daily maximum hourly values and daily

average values [6]. The PM_{10} grid is the hardest to find a suitable compromise and as the number of subscribers grows the suitability of the calculation grid will be reviewed.

Table 2: Pollutants and calculation grid for the CAQI.

Index	Class	Traffic			City Background				
		Mandatory pollutant		Auxiliary pollutant	Mandatory pollutant			Auxiliary pollutant	
		NO_2	PM_{10}	CO	NO_2	PM_{10}	O3	CO	SO_2
Very low	0	0	0	0	0	0	0	0	0
	25	50	25	5000	50	25	60	5000	50
Low	25	50	25	5000	50	25	60	5000	50
	50	100	50	7500	100	50	120	7500	100
Medium	50	100	50	7500	100	50	120	7500	100
	75	200	75	10000	200	75	180	10000	300
High	75	200	75	10000	200	75	180	10000	300
	100	400	100	20000	400	100	240	20000	500
Very High*	> 100	> 400	>100	>20000	> 400	>100	>240	>20000	>500
NO_2, O_3, SO_2: hourly value / maximum hourly value in µg/m3 CO 8 hours moving average / maximum 8 hours moving average in µg/m3 PM_{10} hourly value / maximum hourly value in µg/m3									

* An index value above 100 is not calculated but reported as "> 100"

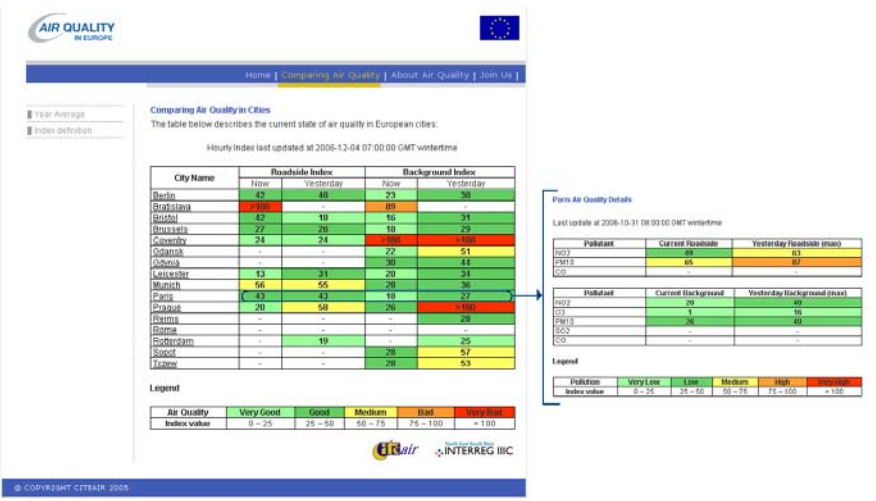

Figure 2: CAQI results for sixteen cities part of the CITEAIR project and details of the CAQI results for the agglomeration of Paris both displayed on www.airqualitynow.eu.

The CAQI resembles the ATMO index discussed above and it differs substantially from for example the UK and US-EPA indices. It therefore shares the drawbacks of the ATMO (no clear link with health effects, fairly arbitrarily quality interpretation of hourly values). But it also shares its advantage: frequently changing index values that capture the hour-by-hour changes and make a website dynamic. The latter was of overriding importance as raising awareness is a key objective of the common website. de Leeuw and Mol [10] compared the CAQI to a number of other indices.

Figure 2 presents how the CAQI is displayed on www.airqualitynow.eu for the 16 current participating cities and the possible comparisons for a given day (e.g. the 4th of December 2006) enabled by the index for two time scales and two types of exposure. As an example, the details of the CAQI calculation for Paris through its sub-indices are also provided.

3.3 A common year average index (YACAQI)

3.3.1 Need for a year average index

Year average indices are not very common in air quality reporting but they are nevertheless a useful indicator for non-experts, facilitating the comparison of cities at a glance. Comparing cities by their individual pollutant levels is difficult as one city might be better on one pollutant and worse on the other. In addition, some cities might monitor other pollutants than others. Even comparing progress in a single city from one year to the other is difficult as progress might be made for one pollutant whereas in another field things might have deteriorated. For example, was the progress on NO_2 more important than the drawback on PM_{10}? How to judge progress in such a case? A year average index is a huge simplification but it does provide an easy way to make some kind of relative assessment on the position of one city to the other or for one city from year to year.

A year average index can be devised according to a concentration grid in the same way as the traditional short-term indices discussed before. Akkan *et al* [11] propose such an index for Baden-Württemberg in Germany (Long-term Air Quality index - LAQx). This index uses long-term exposure (one year) health risks as a guiding principle for classifying air quality. Like the short-term exposure indices, the worst pollutant determines the index. Apart from its methodological merits, health (risks) being the main public concern, this is a very interesting approach.

Another way of making a (long-term) index is the “distance to target” principle. One advantage of the distance to target principle is that each parameter considered contributes to the index (unlike the principle where the worst parameter determines the index). A distance to target indicator calculates, for each pollutant, a ratio of how far the actual measurement is away from the target value, for example a limit value. The overall index/indicator is the average of the sub-indices. A distance to target index is based on policy targets or limit values. The limit and target values have important implications both for environmental policy makers and for the public. Besides, they do have a link to health risks: in Europe they are most of the time related to the recommendations of the World

Health Organisation [12]. The distance to target the way of making an index is the year average index presented in this paper and used on www.airqualitynow.eu.

3.3.2 Calculation and presentation of the YACAQI

Like the hourly and daily index, the Year Average Common Air Quality Index (YACAQI) is calculated for traffic and city background sites. Preferably a city's data for each index is based on the average of a number of sites, however it is up to each city what they want to contribute and how they determine their contribution (monitored or modelled data). The www.airqualitynow.eu website will accept whatever a city submits as their city year average concentrations for each pollutant for traffic and city background situations (or for one of the indices if they do not want to supply both). In most cases, but this is up to individual cities, the data provided to the website will be based on the situation at one or more monitoring sites. This implies that it is not necessarily the complete and balanced picture a city reports under the EU-guidelines. Inferences on city compliance should therefore be based on the official city report and not on the index values on the website as they might not paint the full picture.

The calculation of the sub-indices is detailed in Table 3. Sub-indices are calculated for each pollutant by dividing the actual year average by the EU limit or target value. The overall city index is the average of the sub-indices for NO_2, PM_{10} (both year average and daily averages) and ozone for the city background index. For the traffic year average index the averages of the sub-indices for NO_2 and PM_{10} (both year average and daily averages) are being used. The other pollutants, if data are available, are used in the presentation of the YACAQI but do not enter the calculation of the city average index. They are treated as additional pollutants like in the hourly and daily indices. The main reason is that not every city is monitoring the full range of pollutants. Furthermore for SO_2 we expect that the situation in different kinds of cities is very far apart, being no problem in most cities and a concern in others.

Table 3: Calculation basis for the year average index.

Pollutant	Target value / limit value	Calculation
NO_2	Year average is 40 µg/m^3	Year average / 40
PM_{10}	Year average is 40 µg/m^3 Max. number of daily averages above 50 µg/m^3 35 days ≈ year average of 31 µg/m^3	Year average / 40 Year average / 31
Ozone	25 days with an 8-hour average value >= 120 µg/m^3	# days with 8-hour average >=120 / 25
SO_2	Year average is 20 µg/m^3	Year average / 20
Benzene	Year average is 5 µg/m^3	Year average / 5

Figure 3 presents how the YACAQI is displayed on www.airqualitynow.eu for a selection of cities for two types of exposure, over a number of years.

In addition, it provides the details of the YACAQI calculation for Paris through its associated background sub-indices. This type of presentation provides valuable additional information when comparing two cities or the same city over two years. At a glance it becomes evident what the main problems are and where progress for the situation is satisfactory.

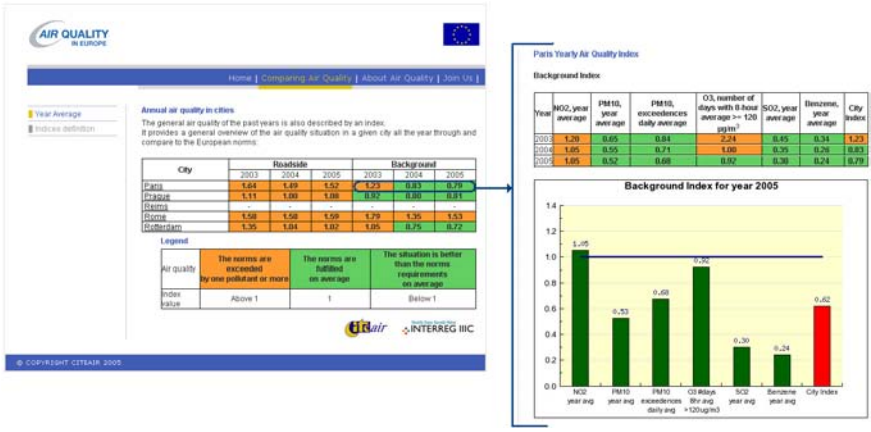

Figure 3: YACAQI results for four cities part of the CITEAIR project and details of the YACAQI results for the agglomeration of Paris (background conditions) both displayed on www.airqualitynow.eu.

Full details on the elaboration of CAQI and YACAQI, as well as sample application, are available in van den Elshout *et al* [6] and on www.airqualitynow.eu. Based on the experiences with their use the indices will be reviewed once at the end of the project, foreseen in 2007. So far PM_{10} appears to be the pollutant posing the greatest challenges in finding a compromise. A potential important change will also be the foreseen arrival of a $PM_{2.5}$ limit value. Further developments of the CITEAIR project will take place in 2007: improvement of the common website, additional participating cities and an assessment of the indices after one year of functioning and peer review. Media will be contacted for a broader information display and a development of the CAQI forecast will be experienced.

4 Conclusion

Cities are engaged in communication with the public, not only because of legal obligations but also to raise awareness. This implies that air quality issues have to be presented in an attractive and educational way. The possibility to compare your own local air quality to a number of other European cities could be an asset in this respect. The purpose of common indices and website is not to replace more detailed local information nor to check EU regulation compliance but to complement it. The value added is to provide, for the first time, a European and

comparable picture of the air quality, near real-time and understandable by anybody. In addition, the provision of separate indices for two types of environmental conditions and three time scales is a methodological innovation. It could also be an alternative to raise public awareness for cities which do not already operate a website.

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Air quality management in Auckland, New Zealand

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Abstract

Air quality in New Zealand is perceived by many to be very good. This is facilitated by low population density, geographical isolation and a maritime climate. The climate and weather of New Zealand is also affected by large scale wind systems which promote westerly winds and aid dispersion.

Despite favourable conditions, air pollution is a problem in many urban centres in New Zealand. Although industrial emissions contribute to pollution, emissions from domestic and traffic sources are significant. Outdoor burning and domestic fires are common, and are a major source of air pollutants and complaints. National Environmental Standards for Ambient Air Quality were introduced in 2004 but these are unlikely to be achieved in a number of locations including Auckland, New Zealand's largest city, where traffic emissions are the major source of air pollution.

Auckland's population is 1.3 million people (almost one third of the national total). The city covers an area approximately equal in size to London. Poorly developed public transport services and urban sprawl have resulted in reliance on private vehicles, and ownership rates in New Zealand are among the highest in the world. In conjunction with an aged vehicle fleet and severe traffic congestion, the resulting air pollution has become a significant issue in Auckland.

This paper considers the process of air quality management in New Zealand, illustrated by the particular problems systemic to Auckland. Policy responses include a Regional Land Transport Strategy with health protection as a key objective. However, it is far from certain whether these will successfully deliver cleaner air, and further national guidance and additional transport focussed regulations may be needed to achieve the air quality improvements in Auckland necessary to meet the national Standards.

Keywords: air quality management, traffic, Auckland, New Zealand.

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1 Introduction

New Zealand is an island nation in the South West Pacific. It is relatively isolated, with Australia as its nearest large neighbour located approximately 2000 km west of New Zealand, across the Tasman Sea. The country has a temperate, maritime climate, which is subject to the large scale wind systems dominating the mid latitudes. The 'roaring forties' winds, an interaction between Antarctic and tropical weather systems, ensure predominant westerly winds affect the length of the country, aiding dispersion in most locations.

New Zealand has a land area of 268,021 km^2 (slightly larger than 241,590 km^2 – the area of the United Kingdom (UK)) and a population of approximately 4.1 million people [1], of which 80% live in cities [2]. The largest of these cities is Auckland, situated on an isthmus in the northern part of the North Island (Figure 1).

The Auckland region is home to approximately 1.3 million people [1]. The urban environment of the region covers about one tenth of the land area, the remainder of which is made up of farmland, coast, and forests.

The population density of the region is 81 people/km^2, much higher than the New Zealand national average of 15 people/km^2 [1], but still relatively low compared to that of Greater London (approximately 4750 people/km^2) or the UK (250 people/km^2). Auckland's intense population growth since European settlement in the 1840s, and particularly since the rise in popularity of the motorcar, has resulted in rapid expansion of the urban area through urban sprawl. Relatively large residential properties and suburban style housing dominate the urban landscape, pushing the urban/suburban boundary and commuting distances further from the centre, and making the provision of efficient public transport increasingly difficult. Despite Auckland's windy coastal environment, transport and domestic emissions cause significant air quality problems across the region: ambient concentrations of nitrogen dioxide and PM_{10} frequently exceed world health organisation guidelines and national standards.

This paper provides a review of air quality management in New Zealand with comparisons to air quality management processes in the UK and Europe with reference to the specific problems experienced in Auckland.

2 Legislative background

The first documented instances of air pollution in New Zealand date back to the 1890s [3]. By the 1950s air quality issues were identified in the city centres of Christchurch and Auckland, relating to odour, industrial emissions, smoky domestic fires and traffic. The Clean Air Act of 1972 authorised the regulation of operations at industrial sites to ensure emissions were minimised by the Best Practicable Means (BPM), a concept first introduced in the UK Alkali Act (1874). The Clean Air Act was administered by the Department of Health, who monitored and investigated emissions from large industries. City and District Councils were responsible for regulation of smaller industries with discharges to air.

Figure 1: Map of New Zealand [4].

2.1 The Resource Management Act (1991)

In 1991, the Resource Management Act (RMA) was introduced; the first legislation for the integrated sustainable management of all New Zealand's natural and cultural resources, and built environment. The RMA is a framework for integrating and rationalising environmental management. It superseded 59 statutes and modified 50 regulations [5]. The RMA turned the focus of environmental management away from the potentially polluting activities, and towards the management of the effects of those activities on the surrounding environment. The role of central Government is to set policy on matters of national significance and monitor implementation of the RMA. Air quality management is carried out by the 12 Regional Councils (and the four Unitary Councils who fulfil the combined responsibilities of Regional and District/City Councils). Air discharge consents are granted by the councils based on compliance of the process with the rules of the respective Regional Plan, and an assessment of environmental effects which must accompany a consent application demonstrating that the application meets the overriding objective of the RMA to *"avoid, remedy or mitigate the effects of activities on the*

environment" [6] In addition to the administration of air discharge consents, Regional Councils are required to monitor the state of the environment, consent compliance, Regional Plan effectiveness, and the outcome of transfers of power (to District Councils). The move of air quality management from central to local government is based on the assumption that governing bodies closest to resources are the most appropriate to govern the use of them [5], and is similar to the approach taken in the UK [7]. In this manner, the specific needs and values of local communities and, in New Zealand, of the native Mäori peoples, are better identified.

Until the adoption of the RMA, air quality monitoring in New Zealand was limited and disorganised. Due to relatively few large industries, and low population density, air pollution was not perceived to be a problem. The advent of the RMA and the requirement for Regional Councils to report on the state of the environment, identified that air quality in New Zealand may not be as good as expected, and that some areas exist where concentrations give reason for concern. To this end, the National Environmental Standards Relating to Certain Air Pollutants, Dioxins, and Other Toxics (NES) were introduced in New Zealand in October 2004 [8].

2.2 National Environmental Standards relating to certain air pollutants, dioxins, and other toxics (2004)

The NES are mandatory standards aimed at protecting air quality which apply nationally. The NES include regulations regarding ambient air quality concentrations (Table 1) and also rules for activities producing discharges to air, such as the burning of oil, operation of incinerators and the use of solid fuel domestic heating appliances. Following the adoption of this legislation, by 1st September 2005 Regional Councils and Unitary Authorities had identified 38 areas where exceedences of the standard were considered likely [9]. These are designated as 'airsheds'.

Table 1: National Environmental Standards [8].

POLLUTANT	STANDARD	TIME AVERAGE	ALLOWABLE EXCEEDENCES PER YEAR	
			NZ	UK / EU
Carbon monoxide (CO)	10 mg/m^3	8-hours (running mean)	1	-
Nitrogen dioxide (NO_2)	200 µg/m^3	1-hour mean	9	18
Ozone (O_3)	150 µg/m^3	1-hour mean	0 - Must not exceed	NA
Fine particles (PM_{10})	50 µg/m^3	24-hour mean	1	35
Sulphur dioxide (SO_2)	350 µg/m^3 570 µg/m^3	1-hour mean 1-hour mean	9 0	24 -

Regional Councils in New Zealand are encouraged to develop airshed action plans to move towards compliance with the fine particle standard by 2013, in relation to PM_{10} which is the standard for which breaches are most likely. Airshed action plans may also be prepared for areas that do not breach the ambient standard – to ensure that this remains the case. An airshed action plan is not a legal requirement of the regulations of the NES, but a strategy to achieve compliance. This is similar to the situation in the UK where local authorities must declare Air Quality Management Areas (AQMA) in locations where pollutant concentrations exceed the air quality objectives. Within 18 months of this declaration, however an Action Plan must be completed. The Action Plan should include details of what measures local authorities are going to introduce, and when, and how these will improve air quality towards meeting the air quality objectives.

The regulations in the NES place different constraints upon the resource consent process depending on the contaminant of concern in the application [9]. Regional Councils are required to publicly report any breaches of the standards on a monthly basis until the standard is no longer breached. With respect to the PM_{10} standard, Regional Councils are required to produce a plan in the form of a 'straight line path' or 'curved line path' from the representative PM_{10} concentration on 1st September 2005 to the standard concentration that should be met by the date included in the regulation – 1st September 2013. If there is a breach of the PM_{10} standard measured within the airshed subsequent to 1st September 2005, the Regional Council must not give consent for further significant discharges of fine particles to air if the discharges are likely to cause concentrations within the airshed to be above the straight line path or curved line path to meeting the standard [8]. Similarly, applications for consent to discharge other contaminants to air, such as carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x) and volatile organic compounds (VOC) are also affected by the NES, and the quality of the air within the airshed directly affects the ability for industry to obtain new or renewed consents to operate within the airshed.

3 Air quality in Auckland

Auckland is New Zealand's largest, most populated city. Although industry is more intensive in Auckland than in any other region in New Zealand, it is transport and domestic emissions that dominate the quality of the air. The Auckland Air Emissions Inventory 2004 estimates [10] show that within the Auckland Region, transport is the principal contributor to ambient concentrations of six pollutants considered in the inventory (Table 2).

Auckland Regional Council operates an extensive ambient monitoring network, including continuous carbon monoxide (CO), sulphur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3), and beta attenuation monitor particulate (PM_{10} and $PM_{2.5}$) analysers. 24-hour medium volume gravimetric PM_{10} and $PM_{2.5}$ monitors are also operated in a number of locations across the region, as well as numerous seasonal studies. This network has been developed over recent

years, and Auckland Regional Council has an increasing understanding of air quality across the region [11].

As required by the NES, due to breaches of the standards, Auckland Regional Council has declared one large airshed covering the entire metropolitan area of the region. Within this airshed, monitoring must be carried out using approved reference methods, in locations identified as potentially worst-scenario locations, in terms of exposure, and intensity or duration of pollution event.

Table 2: Greater London and Auckland Region Emissions [10, 12].

POLLUTANT	TOTAL ANNUAL EMISSIONS (T/YR)		AUCKLAND CONTRIBUTIONS EMISSIONS FROM SOURCE			
	Greater London	Auckland Region	Transport#	Domestic	Industrial	Biogenic
PM_{10}*	3,820	5,900	47%	39%	14%	
NO_x	60,640	35,000	83%	1%	13%	3%
CO	111,645	171,200	85%	13%	2%	
VOC	71,803	64,200	52%	9%	26%	13%
SO_2	1,913	4,200	65%	3%	32%	
CO_2	15,497,385	8,930,000	48%	6%	46%	

* secondary particulates, sea salt, re-suspended dust not included in estimate
\# motor vehicles are responsible for 91% of transport sector emissions

3.1 PM_{10} and NO_2

PM_{10} and NO_2 concentrations in the Auckland Region currently exceed health guidelines and NES standards. Seasonal variation skews the relative concentration of the sources of PM_{10}, and illustrates the significance of particulate from domestic emissions (mainly domestic heating; Figure 2). 63% of households in the region burn solid fuel (mainly wood) for domestic heating [13].

A substantial proportion of domestic particulate emissions are from outdoor burning. Cultural cooking rights of Mäori and Pacific Islanders are maintained throughout the region, and the resulting outdoor, backyard fires are a significant source of particulates and air quality nuisance complaints.

Although domestic emissions in winter are substantially larger than the contribution of traffic emissions of PM_{10} in the region, traffic emissions (including exhaust emissions and tyre and brake wear) are a significant source of PM_{10}. As a product of combustion, the majority of oxides of nitrogen emissions in the Auckland Region are from traffic and industrial sources, as shown in Table 2.

The inventory for the Auckland region indicates that strategies which target emissions from transport and domestic heating will have the greatest impact on improving air quality.

4 Management of target emissions in Auckland

4.1 Domestic heating

The NES includes regulations covering design and thermal efficiency standards of 'woodburners'. The NES refers to woodburners specifically, therefore, other domestic heating units which burn solid fuel and are not called woodburners are not included under this regulation. Coal ranges and open fires are considered the most polluting types of solid fuel domestic heaters, yet are not regulated in this legislation.

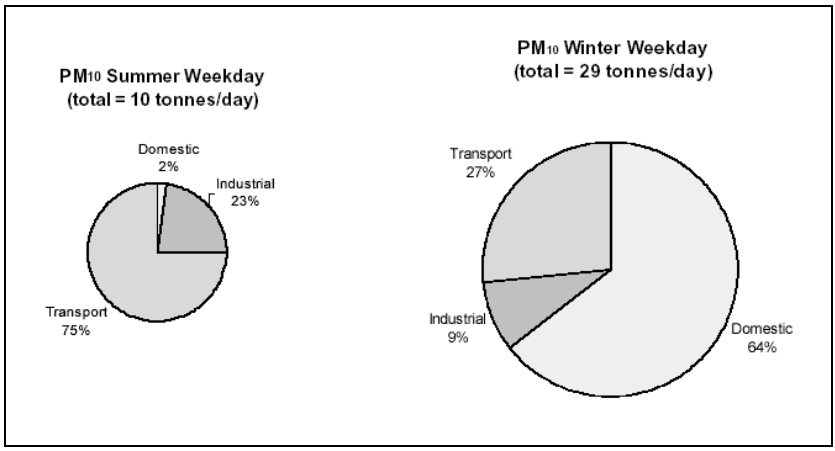

Figure 2: Auckland PM_{10} emissions source contributions [10].

The Auckland Regional Plan includes similar rules regarding the efficiency standards required for new solid fuel domestic heating units installed in homes within the region, and policies regarding the encouragement of clean burning domestic heating methods. However, under the RMA, regulation is carried out on the basis of the effects of the activities, rather than the activity itself. Although there has been some success in regulation of domestic heating appliances in other parts of New Zealand, there is currently no adequate system or legislation in place to regulate the models of solid fuel domestic heaters being installed and operated in Auckland homes.

By comparison, domestic emissions in the UK are managed in a different way. The severe smog events in the 1930s and the catastrophic London Smog of 1952 played an important part in the development of the Clean Air Act (1956) which attempted to control domestic and industrial emissions. The Clean Air Act allowed local authorities to designate 'smoke control areas' where grants to update domestic heating were introduced, and only smokeless fuel could be burned. These areas are still maintained, and local authorities in the UK continue to identify and address potential areas of concentrated domestic emissions via the Local Air Quality Management 'Review and Assessment' process.

4.2 Transport emissions

New Zealand has one of the highest car ownership rates in the world (79 licensed vehicles per one hundred population). There are almost 1 million licensed vehicles in the Auckland Region [14], and approximately 17% of households have access to three or more motor vehicles [15] (compared to only 5% of households in the UK) [16]. The New Zealand traffic fleet age is on average 12 years old [17], equivalent to the technology level of the Euro I vehicle standard, whereas the UK vehicle fleet has an average age of approximately half this [18], equivalent to a Euro II vehicle.

There is no vehicle manufacturing industry in New Zealand and all vehicles are imported. Vehicles are not subject to emissions testing on import into the country, or during regular mandatory warrant of fitness checks. At the time of manufacture, vehicles must have been capable of meeting certain standards. Following a detailed study regarding implementation of emission testing into routine vehicle fitness checks, the Ministry of Transport recently decided that emissions testing will not be introduced in the near future to regulate vehicle emissions in New Zealand [19]. Alternatively, the 'visible smoke test' will be introduced to the warrant of fitness check. The visible smoke test entails a visual assessment of emissions from a vehicle under set conditions. If smoke is emitted for more than five seconds, the vehicle will fail the test until it is tuned or repaired. In addition to the visual smoke test, a prohibition was introduced on the removal of, or tampering with, emission control equipment installed on vehicles, something frequently done in New Zealand in an effort by owners to increase vehicle 'performance'.

The majority of fuel used in New Zealand is produced at a refinery in the North Island subject to the standards imposed by the Ministry of Economic Development. Poor fuel standards in New Zealand have also contributed to the extent of traffic emissions in the country. Benzene and sulphur concentrations in diesel and petrol are high and New Zealand is at least two years behind the EU directives in terms of fuel quality and decreases in pollutant concentration.

Regional councils are required to develop regional land transport strategies that guide the decision making of local authorities. The Auckland Regional Transport Strategy includes the five objectives from the New Zealand Transport Strategy; Assisting Safety; Ensuring Environmental Sustainability; Assisting Economic Development; Improving Access and Mobility; and Protecting and Promoting Public Health, as well as two additional objectives focused on aims specific to Auckland's regional growth and economy. It states that further work beyond the objectives of the strategy will be needed to achieve regionally significant improvements with respect to environmental outcomes [20]. However, the strategy provides an increase in spending on public transport and travel demand management, with a focus on increasing public transport availability in areas identified as regional growth centres. Although positive steps are planned to manage traffic more effectively, as roughly 60-80% of emissions in Auckland come from vehicles (depending on pollutant) [20] it is not certain that this strategy will be sufficient to improve pollution to the necessary levels.

Although the land area of the UK is similar to that of New Zealand, it has a significantly higher population of approximately 60 million, and over 32 million road vehicles. The UK has experienced a considerable increase in vehicle usage (vehicle kilometres rose 79% between 1980 and 2003) and road transport has been the major source attributed to over 90% of the AQMAs declared by UK Local Authorities [21]. However, the increased kilometres travelled have been accompanied by enhanced vehicle abatement technology and other measures, which have assisted in preventing further air quality deterioration. Smaller and cleaner engine size is encouraged through incentives, and vehicles must meet the relevant EU emissions standard. In the UK, regulations are frequently updated to remain up to date with EU directives on vehicle emissions and testing at annual inspections (known as 'MOT's), to ensure that vehicles are maintained and meet required standards.

5 Conclusion

Despite the benefits of low population density and wind, air quality in New Zealand can be poor in urban centres. High vehicle ownership rates, insufficient regulation of fuel quality and vehicle emissions, and significant domestic emissions are culminating in exceedences of the National Standards. These air quality problems are intensified in Auckland, where approximately one third of New Zealand's population live.

The Local Air Quality Management review and assessment process was introduced to the UK under the Environment Act 1995 and subsequent National Air Quality Strategy giving local authorities new powers and obligations, requiring regular assessment of local air quality and integration of air quality management solutions into local policy. This shift was similar to the introduction of the RMA in New Zealand from a technology based approach for controlling emissions to an effects based process for managing ambient air quality. The UK requirements for carrying out monitoring and declaring AQMAs at a local level have been mirrored in the NES by New Zealand, however the production and implementation of action plans is not compulsory..

Although New Zealand has followed similar local air quality management process to the UK, the Auckland emissions inventory suggests that the biggest improvements can still be gained through reductions in transport and domestic emissions. The application of other initiatives implemented in Europe and the UK, such as smoke control areas, and stricter EU emission standards on vehicles, would help to greatly improve air quality in Auckland and across the country.

Acknowledgements

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Simplified reading of one-year air pollution: ranking of chemical and physical variables

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Abstract

This study offers a simple tool to simplify reading of one-calendar-year pollution. Average-concentration and monthly-persistence distributions of chemical pollutants in the troposphere and of meteorological variables are ranked, analysed by means of a non-parametric technique and depicted in a non-parametric space. Sign test is used for ensembles of paired monthly-data related to nitrogen total oxides and ozone, temperature and pressure, continually detected by a survey station of the Network for air-quality control in Rome. Ranks describe atmospheric pollution in one calendar year; pollution is represented in one single graph, where mutual behaviours of variables can be analysed by application of the relational model depending on results of testing paired variables.

As a consequence of this non-parametric combination (ranking chemical and physical atmospheric variables + test) an easy graphic model of pollutant behaviour in one-year climatic oscillations is available.

The current dataset dates back to 1994 since each series was almost complete and meteorological variables were available; moreover, the survey station remained fixed in one position all year long.
Keywords: metropolitan area, Rome, hourly concentration of pollutants, behavioural model.

1 Introduction

Analysis and representation of pollution phenomena in non-parametric spaces is not usual in management of chemical and physical air data; even so, non-parametric tests prove essential for small samples; these tests are common in

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contexts such as psychology [1] and economy and generally in time series analysis [2, 3]. They are well-documented in scientific literature and their powerfulness and efficiency are measured with respect to corresponding parametric tests.

Here a methodological attempt to treat air datasets non-parametrically is accomplished, in order to identify possible significant presences between trends of pollutant concentrations and meteorological variables in one calendar year and, at the same time, to represent such trends in one single graph. This pictorial representation is convenient since graphs play a role of powerful research instruments, from empirical analysis of trends up to choice of forecasting methods [4].

The transformation procedure of quantitative variables into qualitative and, then, the application of the test will be described. Tested samples are small and they are the result of an elaboration of continuous one-calendar-year hourly data acquired by a survey station of the Network for air-quality control in Rome, placed in an area which is characterized by a medium/high density of vehicular traffic, the main source of urban pollution.

2 Materials and methods

2.1 Databases

The database consists of hourly-concentration variables with respect to a) nitrogen oxides and ozone ([concentration], ppb) and meteorological hourly parameters such as b) temperature (T, °C) and pressure (p, hPa). Each variable describes a time series of hourly values. Chemical monitoring data were collected through an automated integration process in one-hour interval (mediation time). The reliability of the chosen dataset has been validated by the Network Administrator; hence, data have been accepted and accounted as believable [5], in step with current epistemological literature [6].

NO_x represents the total amount of NO, NO_2 and other nitrogen oxides.

High-temperature combustion processes, like those occurring in piston-engines, are the main NO_x anthropic-source. NO_x play a key-role in O_3 formation. Both of them are reactive pollutants.

2.2 Preprocessing

First Student's t-test [7] was applied to check normality of each distribution relating to the corresponding time series of chemical-pollutants hourly-concentrations; all distributions proved normal at 95%. The initial size of each pollutant distribution turned out not to be smaller than 85% of the expected yearly one on average.

Anyway, corresponding time series showed gaps caused by bad working of analysers; in order to complete them, data-filling was needed. To perform it, suitable working matrices, transposed with respect to the original sample, were used. Hourly-concentration values of all pollutants in one month (720X1) were analysed within 24 h x 30 days matrices to which interpolation and forecasting

techniques [8] were opportunely applied. This way more than 10% of missing chemical data in pollutant distributions were recovered. The size of meteorological-variable distributions was about 95% of theoretical one, with no need of reconstruction.

2.3 Statistical description of monthly series of hourly values

Each time series of hourly-concentration values and meteorological variables with respect to each month in one year was described statistically [9] by means of its arithmetic mean, median, confidence interval for the mean, quartiles, standard deviation and variance (s^2). Since time series were under examination, monthly means and variances for every variable were chosen as working parameters. As known, variance describes statistical dispersion (spreading) around the expected value and allows the experimenter to know how one variable depends on another (autoregression) [10]. By means of variance the persistence or stationarity of the series can be determined; in this context this parameter is used to monitor the one-year trend of each monthly variable since it is a measure of how probable is a process in a particular time interval (one month in this case), if the same is observed in the previous one.

Monthly values of each mean and persistence distribution were normalized with respect to their one-year averages. Results are shown in Table 1.

Table 1: Parametric monthly statistics of chemical and physical parameters continually monitored by a survey station of the Network for air-quality control in Rome

	NO_x	NO_x	NO_2	NO_2	O_3	O_3	T	T	p	p
units	ppb	ppb	ppb	ppb	ppb	ppb	°C	°C	hPa	hPa
	m	s^2	m	s^2	m	s^2	m	s^2	m	s^2
Jan	1,14	19,94	0,75	0,84	0,65	0,07	0,56	0,66	1,0002	2,06
Feb	0,98	11,40	0,89	0,77	0,28	0,09	0,52	0,99	0,9993	1,27
Mar	1,02	9,59	1,06	1,29	0,69	0,53	0,79	0,81	1,0044	0,71
Apr	0,80	4,86	0,95	1,04	0,77	0,28	0,78	1,06	0,9949	1,48
May	0,94	3,62	1,10	0,61	1,26	1,06	1,16	1,28	0,9971	0,45
Jun	0,75	4,41	1,12	1,07	1,48	1,75	1,34	1,30	0,9992	0,27
Jul	0,63	3,56	1,08	1,21	1,79	3,17	1,68	1,06	0,9961	0,10
Aug	0,53	2,43	0,96	0,98	2,02	3,29	1,68	1,08	0,9969	0,31
Sep	0,76	5,03	0,96	1,05	1,38	1,11	1,38	1,05	0,9988	0,41
Oct	1,04	13,25	0,94	1,18	0,93	0,46	1,03	1,08	1,0005	1,39
Nov	1,82	22,54	1,09	1,06	0,74	0,08	0,51	0,85	1,0062	1,51
Dec	1,60	19,36	1,12	0,90	0,46	0,10	0,57	0,78	1,1341	2,05
1-yr values	118,8	10532,2	41,3	333,3	9,9	92,0	16,6	1,00	1032,2	1,00

m = mean ; s^2 = variance

Monthly values are normalized with respect to one-year averages

2.4 Procedure for transforming and constructing the sample

Each quantitative value in each distribution, of means and variances in sequence, is assigned a rank [1] 1 to 12 (since months are 12 in one year), according to its magnitude. Assignment can proceed either in increasing or decreasing order. In case of *ex-aequo* values, first value is assigned its suitable rank, second one the following rank and so on; all assigned ranks are added and the sum is divided by the number of equivalent cases which were found, so getting a final rank to be assigned to the whole of *ex-aequo* values. Ranks of each monthly variable over one calendar year are shown in Table 2 (means and variances in sequence).

Table 2: Non-parametric statistics of chemical and physical variables.

	NO_x	NO_x	NO_2	NO_2	O_3	O_3	T	T	p	p
	r_m	r_{s2}	r_m	r_{s2}	r_m	r_{s2}	r_m	r_{s2}	r_m	r_{s2}
Jan	11	11	1	3	3	1	3	1	8	12
Feb	10	8	2	2	1	3	2	5	7	7
Mar	7	7	7	12	4	7	6	3	10	6
Apr	8	5	4	6	6	5	5	7,5	1	9
May	5	3	10	1	8	8	8	11	4	5
Jun	6	4	12	9	10	10	9	12	6	2
Jul	3	2	8	11	11	11	11	7,5	2	1
Aug	2	1	5,5	5	12	12	12	9,5	3	3
Sep	1	6	5,5	7	9	9	10	6	5	4
Oct	4	9	3	10	7	6	7	9,5	9	8
Nov	9	12	9	8	5	2	1	4	11	10
Dec	12	10	12	4	2	4	4	2	12	11

r_m = rank for mean ; r_{s2} = rank for variance

In order to identify significant differences between variable distributions, the latter have to be paired and members in each pair must be mutually classified, taking account of sign-differences. Sign distributions (either > or <) are obtained; possible *ex-aequo* distributions are removed. This way binomial distribution suitably describes probability of a plus (>) or a minus (<) occurrence. Sum over all signs is a measure of sample dimension, while sum over less frequent sign is used as a row-value in the probability-table.

2.5 Sign test

In sign test [1] the cumulative function of statistical distribution is independent of observation one; if observations in two ensembles are distributed according to the same cumulative function (not specified), null hypothesis (H_0) proves true

[11]. Sign-test powerfulness and efficiency are 95% for small samples, but they decrease at increasing of sample dimension, until they reach the asymptotic value of 63% for large ones [12].

In statistical hypothesis testing, the p-value (significance) is the probability of obtaining a result at least as extreme as that obtained, assuming the truth of the null hypothesis that the finding was the result of chance alone.
Null hypothesis (H_0) corresponds to:

$$p\,(X_A > X_B) = p\,(X_A < X_B),$$

i.e. probability p of having distribution X_A larger than X_B equals that concerning the inverse case.

The significance level (α) is the probability that the null hypothesis will be rejected in error when it is true; generally, one rejects the null hypothesis if the p-value is smaller than or equal to the significance level. Here $\alpha = 0.05$ (significance at 5%); when $\alpha > p$, H_0 is rejected and the finding is said to be 'significant at the 5% level'. In other words, rejecting H_0 is equivalent to say a significant difference exists in the behaviour of the two distributions.

2.6 Sampling

From one-year distributions, both for ranks of mean values and of monthly-persistence of pollutant-concentrations and meteorological values, the corresponding distributions relating to periods:

- spring–summer (April–September); sample dimension = 6
- fall–winter (October–March); sample dimension = 6
- 'school-time' (October–June); sample dimension = 9

were extracted.

The first two periods were chosen since the maximum (minimum) of one of meteorological variables describing climatic oscillations in the Mediterranean area falls in one of them and the minimum (maximum) in the other. The third period was chosen as a marker of anthropic activity in the urban area, decreasing July to August since didactics is interrupted and people are on vacation. In each period all paired variables were checked under the hypothesis H_0 was true.

Table 3 holds mean and persistence pairs of those variables whose distributions proved significant under test application, together with associated probabilities.

Fig. 1 shows a graphic model of parameter interrelation, which was carried out taking account of sign-differences among distribution-pairs, i.e. rank distributions.

One-year trends of monthly-means of NOx, NO_2, O_3, T and p are drawn in Fig. 2.

Table 3: Results of applying sign test to pollutant and meteorological variable pairs collected in one calendar year in Roman urban area.

	spring–summer period April–September		fall–winter period October–March	
Variables	p_m	p_s^2	p_m	p_s^2
$NO_x \leftrightarrow O_3$	**0,016**	**0,031**	**0,016**	**0,031**
$NO_x \leftrightarrow NO_2$	**0,031**	0,109	**0,031**	0,344
$NO_x \leftrightarrow T$	**0,016**	**0,031**	**0,016**	0,109
$NO_x \leftrightarrow p$	0,181	0,656	**0,031**	0,344
$NO_2 \leftrightarrow p$	**0,016**	0,344	**0,016**	0,344
$O_3 \leftrightarrow p$	**0,016**	0,109	**0,016**	*
$p \leftrightarrow T$	**0,016**	0,109	**0,016**	0,656

Variables: pairs showing significant differences in r_m and/or r_s trends are reproduced.

p_m = p-value for mean, p_s^2 = p-value for variance.

Significant differences are written in bold.

Probabilities are calculated according to tables available in [1].

**-symbol stands for' no value', when sample dimension is smaller than 5.*

Figure 1: Behavioural model of reactive pollutants in the climatic oscillations.

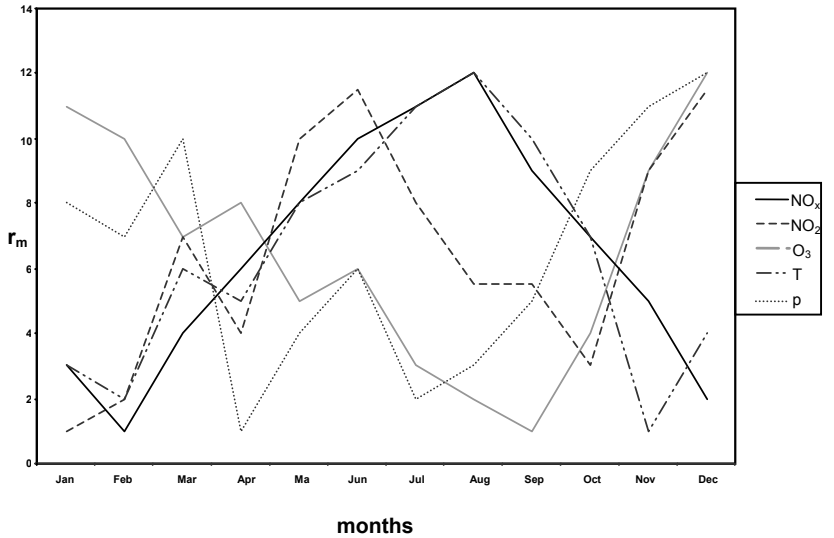

Figure 2: Trends of pollutants and meteorological variables in one calendar year.

3 Results and discussion

Statistical hypothesis testing tells apart two different situations: either the absence of significant differences or a marked dominance of one sign on the other; this means a different behaviour among pollutants and between pollutants and the other physical parameters.

Looking at Table 3, it is evident how physical-parameter behaviours (temperature and pressure) change significantly during climatic oscillations.

Temperature and pressure control processes relating to photo-chemical pollutants such as O_3 and NO_x both in spring-summer period and in fall-winter one. In both periods O_3 and NO_x are significantly and inversely connected: in the former interval NO_x decreases at increasing of temperature and ozone-concentration [13–16], while it increases at decreasing of the same chemical-physical parameters in the latter one; in both periods the corresponding trends prove not mutually stationary.

Pressure controls NO_2 and O_3 behaviours in both terms; no significant difference exists between respective stationarities, but just between trends of mean-values. Note the relation between NO_x and p is only significant in fall-winter period ($p = 0.031 < \alpha = 0.05$), not since the pollutant increases at decreasing of pressure, but because of oscillations in trends of NO_2, which show the same stationary tendency ($p = 0.344 > \alpha = 0.05$). It is reasonable to assert climatic oscillations control reactive processes, which prove specular in the two cycles. Trends mutually cancel out in these two periods, as it was pointed out by test results, which found no significant differences between 12-month trend pairs.

All pollutants show the same expected behaviour: no significant differences, not only within one calendar year, but also during 'school-time'. This suggested the three summer months, removed from analysis because of reduced traffic, are not able to generate a different behaviour with respect to the entire year.

NO_x-trend (Fig. 2) increases September up to November, when absolute maximum is reached, and decreases June to August (absolute minimum) [17]. NO_2 doesn't follow oxide-trend, but rather pressure, even if such a behaviour is reversed in June-July. In fact, from this period up to December, NO_2 mean-concentration increases more rapidly than pressure, while January to June the reverse happens. O_3 follows temperature curve.

4 Conclusions

This procedure, quickly automatable, allows the researcher to compare pollution events in different temporal situations at different latitudes. Moreover, according to data-management finalities, it can be extended to other chemical variables such as benzene and polycyclic aromatic hydrocarbons, but also vehicular-traffic fluxes, emissions and so on; in short, to all variables contributing to atmospheric pollution in urban and industrial areas (provided the sample dimension is smaller than 25). Of course, the present scientific results are nor exhaustive, but they're not in contradiction with known outcomes from parametric statistical techniques.

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SO_X emission reduction in the ceramic industry: BAT and beyond

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Abstract

The ceramic industry in Flanders (Belgium) consists of ca. 30 plants producing mainly bricks, but also roof tiles, vitrified clay pipes and expanded clay aggregates. The clay minerals that are used as raw materials in these plants often contain high levels of sulphur. As a result, the ceramic industry is an important source of SO_X emissions in Flanders. In 2004, the SO_X emissions of the ceramic industry were estimated at 11,247 ton, or more than 10% of the total SO_X emissions in Flanders. In order to meet the objectives of the EU NEC-Directive (2001/81/EC), the Flemish authorities aim at reducing the SO_X emission of the ceramic industry to 5,460 ton by 2010.

In this context, the Flemish authorities (Flemish Institute for Technological Research) asked VITO to determine the Best Available Techniques (BAT) for reducing SO_X emissions in the ceramic industry. The selection of the BAT was based on a detailed evaluation of different emission reduction measures, such as addition of low sulphur and/or Ca-rich raw materials and different end-of-pipe techniques. Aspects that were considered in the evaluation of the measures included: technical applicability, achievable SO_X emission levels, cross-media aspects and associated costs. SO_X emission limit values were suggested based on the BAT selection and the associated SO_X emission reductions were estimated. The analysis showed that application of BAT cannot guarantee the Flemish ceramic industry reaching the desired SO_X emission level of 5,460 ton SO_X in 2010. Therefore, the study also examined strategies that go beyond BAT, in order to achieve further emission reductions.

Keywords: ceramic industry, SO_X emissions, Best Available Techniques, IPPC-Directive, NEC-Directive.

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1 Introduction

The IPPC-Directive (96/61/EC) [1] has introduced a framework requiring EU Member States to issue operating permits for industrial installations carrying out activities described in Annex 1 of the directive. These permits must contain conditions that are based on 'Best Available Techniques' (BAT), in order to achieve a high level of protection of the environment as a whole. BAT are defined as technologies and organisational measures that minimise the overall environmental impact and are available at an acceptable cost (cf. art. 2).

In Belgium environmental permit legislation is part of the individual competency of the three regions: Flanders, Wallonia and Brussels Capital Region. In Flanders, the environmental legislation lists the activities that require an environmental permit (broader than Annex 1 of the IPPC Directive) and includes the procedures to obtain such a permit. It also contains a list of general conditions, sectoral conditions per industry and emission limit values that should be used as minimum conditions in granting environmental permits. Environmental permit conditions should be based on (i) BAT, and (ii) local environmental quality objectives. The translation of BAT into permit conditions is usually carried out at sector level. The sectoral emission limit values are based on sectoral BAT.

In 1995, the Flemish government established a dedicated BAT-centre within VITO (Flemish Institute for Technological Research). The BAT-centre selects BAT at sector level and supports the authorities and the companies to put BAT into practice for many industrial activities [2]. One of the more recent reports published by the BAT-centre deals with the BAT for reducing the SO_X emissions of the ceramic industry in Flanders. The methodology and main conclusions of this report are presented in this paper.

2 SO_X emissions of the ceramic industry in Flanders

The ceramic industry in Flanders consists of ca 30 plants producing mainly bricks, but also roof tiles, vitrified clay pipes and expanded clay aggregates. The clay minerals used as raw materials in these plants often contain high levels of sulphur. As a result, the ceramic industry is an important source of SO_X emissions in Flanders.

For the purpose of the BAT analysis, the Flemish ceramic industry is divided into four groups, based on the S-content of the raw materials:

- Group 1: < 0.25 % S (11 plants, 30 production lines);
- Group 2: 0.25-0.50 % S (3 plants, 4 production lines);
- Group 3: 0.50-0.75 % S (5 plants, 7 production lines);
- Group 4: > 0.75 % S (9 plants, 14 production lines).

Based on data reported by the plants in their annual environmental reports, the total SO_X emissions of the Flemish ceramic industry in 2004 are estimated at ca 11,247 ton, which is more than 10% of the total SO_X emissions in Flanders. As shown in Figure 1, more than 85% of the total SO_X emissions of the Flemish

ceramic industry originate from plants in group 3 and 4. This is explained by the strong correlation between the S-content of the raw materials and the SO_X emission levels.

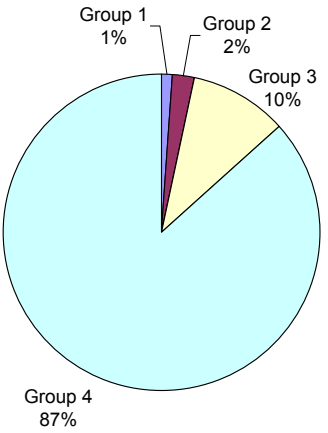

Figure 1: Contribution of the different groups to the total SO_X emissions of the Flemish ceramic industry in 2004 (based on data reported by the plants in their annual environmental reports).

In order to meet the objectives of the EU NEC-Directive (2001/81/EC) [3], the Flemish authorities aim at reducing the SO_X emissions of the ceramic industry to 5,460 ton by 2010. This is equivalent to an emission reduction of 51.5 % compared to 2004.

In this context, the Flemish authorities asked VITO (Flemish Institute for Technological Research) to determine the BAT for reducing the SO_X emissions of the ceramic industry. The BAT-study aims at:

- evaluating the different abatement measures for reducing the SO_X emissions of the Flemish ceramic industry and selecting the BAT (see paragraph 3);
- suggesting BAT based emission limit values (ELV's) for the sector and estimating the reduction of SO_X that can be reached by applying BAT (see paragraph 4);
- proposing and assessing strategies/scenarios that go beyond BAT, in order to achieve further emission reductions (see paragraph 5).

3 Evaluation of abatement measures and BAT selection

According to the IPPC Directive [1], European member states are required to take BAT into account when determining permit conditions, e.g. emission limit values. The BAT for the ceramic industry are discussed in the European BAT Reference Document (BREF) on the Ceramic Industry [4]. In this paper, the

BAT for SO_X emission reduction in the ceramic industry are determined for the Flemish situation. The methodology for the BAT selection is described in [2] and includes an evaluation of different candidate BAT with respect to their technical feasibility, environmental benefit and economic aspects.

3.1 Abatement measures considered in the evaluation

Both process integrated measures and end-of-pipe techniques are considered in the BAT evaluation for the Flemish ceramic industry.

3.1.1 Process integrated measures

According to the BREF [4], several process integrated measures are considered as BAT for reducing SO_X emissions in the ceramic industry [4]. The following abatement measures are evaluated for the ceramic industry in Flanders:

- the use of low sulphur fuels, e.g. natural gas;
- optimisation of the heating curve;
- in the case of sulphur rich raw materials: addition of low sulphur body additives (e.g. sand) or low sulphur clay to the raw materials;
- in the case of sulphur rich raw materials: addition of Ca-rich additives to the raw materials.

Practical experience in the Flemish ceramic industry has shown that up to 25% of the sulphur rich raw materials can be substituted by low sulphur and high calcium materials (e.g. loams). Higher substitution degrees result in insufficient product quality (decreased product strength). Another factor limiting the applicability of these measures is the availability of low sulphur and high calcium loams. The latter is related to social and environmental acceptance of additional loam pits in Flanders.

3.1.2 End-of-pipe techniques

Different end-of-pipe techniques can be considered for reducing SO_X emissions in the ceramic industry [4]. The following abatement measures are evaluated for the ceramic industry in Flanders:

- cascade type packed bed adsorbers (adsorption of SO_X on a packed bed of $CaCO_3$ granules);
- dry flue gas cleaning with a filter (adsorption of SO_X on $CaCO_3$ powder that is blown into and subsequently filtered from the flue gas stream);
- wet or semi-wet flue gas cleaning (absorption of SO_X in an alkaline water phase).

Both cascade type packed bed adsorbers and dry flue gas cleaning with a filter are considered as BAT in the BREF [4]. Wet or semi-wet flue gas cleaning is not generally considered as BAT because of the cross-media effects and the high investment and maintenance costs.

3.2 Technical feasibility and environmental benefit

3.2.1 Currently applied emission reduction techniques

The assessment of the currently applied emission reduction techniques is based on information received from ca. 30 production lines in the Flemish ceramic

industry. As a result of a new emission regulation that came into force in Flanders in 2004, most of these plants recently implemented emission reduction techniques. The applied techniques and the achieved SO_X emission levels are summarised in Table 1. Apart from SO_X emission reduction, the implemented measures also result in reduction of HF emissions, which will not be discussed in this paper.

Table 1: Applied techniques and achieved SO_X emission levels in Flemish ceramic plants.

	% S in the raw materials	Implemented emission reduction technique(s)	SO_X-emissions (mg/Nm³)	
			before implementation of the emission reduction technique(s)	after implementation of the emission reduction technique(s)
Group 1	< 0.25%	cascade type packed bed adsorbers	18-233	5-186
Group 2	0.25-0.50%	no data available	no data available	no data available
Group 3	0.50-0.75%	cascade type packed bed adsorbers combined with primary measures	247-1938	99-998
Group 4	> 0.75%	cascade type packed bed adsorbers combined with primary measures, or dry flue gas cleaning with filter	425-3376	71-2192

3.2.2 Possible additional emission reduction techniques

For groups 1 and 2, no additional emission reduction techniques need to be considered, since the contribution of these groups to the total SO_X emissions of the ceramic industry is very limited (see Figure 1). For groups 3 and 4, the following additional emission reduction techniques can be considered:

- for plants equipped with a cascade type packed bed adsorber: use of a modified type of $CaCO_3$ adsorbent with higher SO_X adsorbing efficiency;
- for plants equipped with dry flue gas cleaning with filter: increase of the amount of $CaCO_3$ that is blown into the flue gas stream;
- for all plants: switch from dry flue gas cleaning to wet or semi-wet flue gas cleaning.

3.2.3 Achievable SO_X emission reduction

Since the additional abatement techniques are not yet applied in Flanders, the achievable SO_X emission levels are estimated based on literature data [4] and suppliers' information (see Table 2).

3.3 Economic aspects

Economic aspects play an essential role in the BAT selection, since a BAT should be 'available' under economically viable conditions. In order to evaluate

the economic feasibility of the different emission reduction techniques, the total annual costs are calculated for a hypothetical 'average' company. For the techniques that are already implemented (see paragraph 3.2), the cost calculations are based on actual cost data. For the additional techniques to be considered (see paragraph 3.3) the cost calculations are based on suppliers' information and own calculations (e.g. for adsorbent consumption). Figure 2 shows the total annual costs for the different emission reduction techniques for an 'average' company in group 4.

Table 2: Achievable SO_X emission levels in Flemish ceramic plants after implementation of additional emission reduction techniques.

	% S in the raw materials	Additional emission reduction technique	Achievable SO_X-emissions (mg/Nm³)
Group 3	0.50-0.75%	cascade type packed bed adsorbers (modified $CaCO_3$) combined with primary measures	< 500 mg/Nm³
		wet or semi-wet flue gas cleaning	< 500 mg/Nm³
Group 4	> 0.75%	cascade type packed bed adsorbers (modified $CaCO_3$) combined with primary measures or dry flue gas cleaning with filter (increased amount of $CaCO_3$)	< 850 mg/Nm³
		wet or semi-wet flue gas cleaning	< 500 mg/Nm³

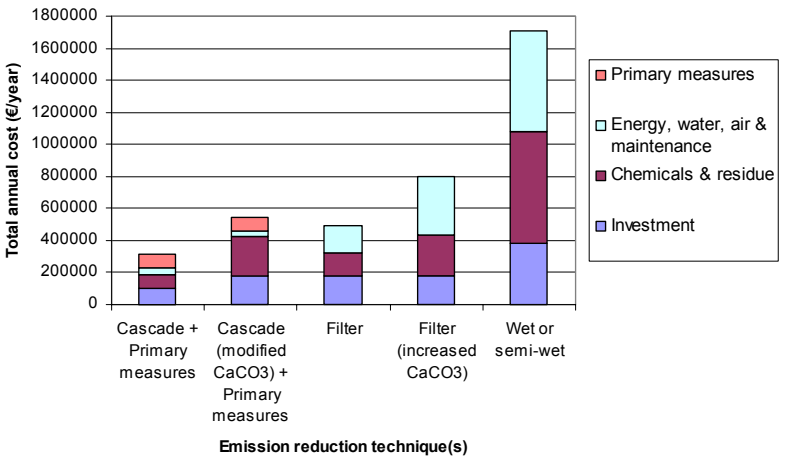

Figure 2: Total annual costs of different emission reduction techniques for an average company in group 4.

In Figure 2, the total annual costs are split into:

- investment costs: annual investment costs for end-of-pipe techniques as well as for primary measures (if the latter are relevant);

- chemical and residue costs: costs related to adsorbent or absorbent consumption, disposal or processing of used adsorbent or absorbent streams;
- energy, air, water and maintenance costs;
- costs of primary measures: additional costs for low sulphur and high calcium materials (if relevant).

These total annual costs are compared to the turnover, profits and added value of a hypothetical 'average' company. Using the indicative reference values in Table 3 combined with expert judgement, the economic feasibility of the different techniques is assessed (see Table 4).

Table 3: Indicative reference values for economic feasibility [5].

Compare total annual costs to …	Acceptable	To be judged	Not acceptable
turnover	< 0.5%	0.5-5%	> 5%
profits	< 10%	10-100%	> 100%
added value	< 2%	2-50%	> 50%

Table 4: Assessment of the economic feasibility of the different emission reduction techniques for an average company in group 4.

Emission reduction technique	Already applied in Flanders?	Total annual cost as a percentage of …			Global assessment of economic feasibility
		Turnover	Profits	Added Value	
Cascade type packed bed adsorbers combined with primary measures	Yes	2.96% (to be judged)	8.39% (to be judged)	n.a.*	Feasible
Cascade type packed bed adsorbers (modified $CaCO_3$) combined with primary measures	No	5.16% (not acceptable)	14.66% (to be judged)	n.a.*	Limited
Dry flue gas cleaning with filter	Yes	4.64% (to be judged)	13.16% (to be judged)	n.a.*	Limited
Dry flue gas cleaning with filter (increased amount of $CaCO_3$)	No	7.55% (not acceptable)	21.44% (to be judged)	n.a.*	Limited
Wet or semi-wet flue gas cleaning	No	16.06% (not acceptable)	45.60% (to be judged)	n.a.*	Not feasible

*: the average added value for the years 2000-2003 was negative.

3.4 BAT conclusions

Based on the evaluation in paragraphs 3.2 and 3.3, it may be concluded that the BAT for reduction of SO_X emissions in the Flemish ceramic industry is a combination of primary measures and end-of-pipe techniques:

- Primary measures:
  - The use of low sulphur fuels, e.g. natural gas;
  - Optimisation of the heating curve;
  - In the case of sulphur rich raw materials: addition of low sulphur body additives (e.g. sand) or low sulphur clay to the raw materials;
  - In the case of sulphur rich raw materials: addition of Ca-rich additives to the raw materials.
- End-of-pipe techniques:
  - cascade type packed bed adsorbers with standard or modified $CaCO_3$; or
  - dry flue gas cleaning with a filter.

Wet or semi-wet flue gas cleaning is not generally considered as BAT, because of the cross-media effects and the high investment and maintenance costs. These techniques can however play a role in scenarios that reduce the SO_x emissions of the ceramic industry in Flanders beyond the levels that are achievable with BAT (see paragraph 5).

4 BAT based ELV's and associated SO_x emissions

By applying BAT as defined in paragraph 3.4, ceramic plants in groups 1, 2 and 3 should be able to comply with an emission limit value (ELV) of 500 mg/Nm³. For plants in group 4 however, an ELV of 500 mg/Nm³ can only be met by applying wet or semi-wet flue gas cleaning, which is not BAT. For this group an ELV of 1,000 mg/Nm³ is judged to be in accordance with BAT.

Primary measures (addition of low sulphur, calcium rich materials) play an essential role in meeting these ELV's, especially for plants in groups 3 and 4. As discussed in paragraph 3.1.1, the applicability of these measures to the Flemish ceramic industry is limited by the availability of low sulphur and high calcium loams. This is related to the limited social and environmental acceptance of additional loam pits in Flanders. In scenarios with very limited availability of loam, ELV's up to 1,500 mg/Nm³ are judged to be in accordance with BAT, as is shown in Table 5.

Table 5: Scenarios with BAT based ELV's.

	Scenario	BAT-sufficient loam availability	BAT-limited loam availability	BAT-very limited loam availability
Emission limit value (mg/Nm³)	Group 1	500	500	500
	Group 2	500	500	500
	Group 3	500	750	1000
	Group 4	1000	1250	1500
Total SO_X emissions (kton/year)		5.80	7.12	8.29

Table 5 also shows the total SO_X emissions that will be attained by the Flemish ceramic industry if the plants comply with the proposed ELV's. These total SO_X emissions are calculated based on SO_X emission and concentration data reported by the individual plants in 2004, using the following formula:

$$SO_{X\ BAT}\ (kg) = \frac{ELV_{BAT}\ (mg/Nm^3)}{SO_X\ concentration_{2004}\ (mg/Nm^3)} \times SO_{X\ 2004}\ (kg)$$

Table 5 shows that, by imposing BAT based ELV's, the SO_X emissions of the Flemish ceramic industry can be reduced to 5.80 kton/year in the best case (i.e. when assuming sufficient loam availability). These BAT based ELV's do not allow to reach the maximum of 5.46 kton which was set as a goal for the ceramic industry in 2010 by the Flemish authorities, in order to reach the objectives of the EU NEC-Directive.

5 Scenarios beyond BAT

In order to reach the objectives of the EU NEC Directive [3], abatement measures beyond BAT will need to be implemented. Two basic types of scenarios can be considered:

- Scenarios with sectoral ELV's beyond BAT;
- Scenarios with BAT-based ELV's, in combination with voluntary agreements to reach further emission reductions in a limited number of plants.

An example of a scenario with sectoral ELV's beyond BAT is presented in Table 6. In this scenario, plants in group 4 implement emission reduction measures beyond BAT in order to meet the imposed ELV. In theory, this scenario would decrease the total SO_X emission of the Flemish ceramic industry to 4.63 kton per year, which is well below the goal of 5.46 kton. However, this scenario is expected to have undesirable socio-economic consequences, with possibly several plants in group 4 closing down, because the required emission reduction measures are not economically feasible for an 'average' company.

Table 6: Scenarios with ELV's beyond BAT.

	Scenario	Beyond BAT
Emission limit value (mg/Nm^3)	Group 1	500
	Group 2	500
	Group 3	500
	Group 4	750
Total SO_X emissions (kton/year)		4.63

The emission goal of 5.46 kton can also be reached by imposing BAT-based ELV's on the sector as a whole, in combination with the implementation of wet or semi-wet flue gas cleaning in a limited number of plants in group 4. These plants should preferably be large plants with very high SO_X emissions. In such plants, emission reduction measures that go beyond BAT for the sector as a whole, can be implemented under more economically feasible conditions. Table 7 lists some potential scenarios and the associated SO_X emissions. Scenarios such as those in table 7 can be stipulated in voluntary agreements between the industry and the authorities. Compared to scenarios with sectoral

ELV's beyond BAT (Table 6), these scenarios offer a more realistic option to reach the emission reduction goal for the sector under economically feasible conditions and without unacceptable socio-economic consequences.

Table 7: Scenarios with BAT based ELV's and implementation of techniques beyond BAT in a limited number of plants.

	Scenario	BAT*	BAT*	BAT*
Emission limit value (mg/Nm^3)	Group 1	500	500	500
	Group 2	500	500	500
	Group 3	500	750	1000
	Group 4	1000	1250	1500
Number of plants with wet or semi-wet flue gas cleaning		1	2	3
SO_X emissions (kton/year)		5.03	5.29	5.25

6 Conclusions

Due to the high sulphur content of raw materials, the ceramic industry is an important source of SO_X emissions in Flanders. In order to reach the goals set by the European NEC-Directive, significant SO_X emission reductions are required. Implementation of BAT, which is a combination of primary measures and dry flue gas cleaning techniques, is not sufficient to reach the required emission reductions. Compared to scenarios with sectoral ELV's beyond BAT, voluntary agreements between industry and authorities offer a more realistic option to reach the emission reduction goal for the sector under economically feasible conditions and without unacceptable socio-economic consequences.

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[2] Dijkmans R., *A transparent and proven methodology for selection of Best Available Techniques (BAT) at the sector level by guided expert judgement*, Journal Cleaner Production - vol. 8 (1): pp. 11-21, 2000

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Pollutants site ratio as appointment of highway, industrial and farming sources

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Abstract

An in-situ field study was conducted to measure the outdoor pollutant concentrations necessary to design the ventilation-filtration system and improve the indoor air quality of a public building. The area of study is located in the flat terrain of the Italian Po valley, near a traffic-congested highway and surrounded by an industrial factory and many farms. The quality of the ambient air was evaluated monitoring NO_2, toluene and xylenes concentrations, and was compared with that in urban atmospheres and related to traffic emissions. Measurements of pollutant were performed with passive diffusion samplers with the aim to test the hypothesis that the highway contribution to ambient air quality varies with the logarithm of the distance. The toluene/xylenes ratio measured at the building site and at the highway source ratio suggested that beside vehicular emission, industrial and farming sources were governing the volatile organic compounds in the area. The present study confirmed that NO_2 concentration at a nearby highway varied linearly with the logarithm of the distance from the highway, but the slope found for this regression was somewhat steeper than those reported in the literature for urban conditions. The reason for this has not been related to augmented atmospheric dispersion differences. Instead, the presence of hydroxyl radicals and volatile organic compounds of either agricultural or industrial origin may affect a complex ozone-hydrocarbon reactivity. The results delineate the pollutant site ratio and the traffic equivalent distance as useful parameters for the source emissions characterisation and the selection of an effective control technology.
Keywords: traffic emissions, environmental profiles, source emission ratio, equivalent distance, V.O.C. reaction kinetic.

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1 Introduction

In the context of a study on highway emissions facing a residential area under construction, a series of gradient measurements of NO_2, SO_2, O_3 and VOC concentrations with increasing distance from the highway were performed using passive diffusion samplers. In recent papers results showing a logarithmic relationship between NO_2 concentration and distance from the highway have been presented [1–3]. Such relationship can be useful in outdoor-indoor air quality relationship, when the distance to major roads is sometimes used to estimate pollution level, and the degree of air purification needed to obtain the desired indoor air quality is required. It is however essential to test the general validity of these relationships using data from different geographical areas and also to extend the research to other traffic related volatiles pollutants like benzene, toluene and xylenes and other aromatic hydrocarbons. The small-scale spatial variability of air pollution observed in urban areas has often created concern about the representativeness of measurements used in exposure studies for risk assessment. In the literature there are a relatively high number of articles published on the concentration of some of the important urban pollutants and the main anthropogenic sources. However most of the studies have been focused on the determination of their absolute concentrations with hot-spot samplings. More valuable information can be gained from measurements in which the time weighted average (TWA) concentrations are determined because these are much less susceptible to instantaneous variations of local conditions. Diffusive sampling then becomes an ideal method to determine concentrations for prolonged sampling times because of the possibilities of unattended operations, ease of handling and an overall low-cost [4]. Although TWA concentrations are more significant in terms of atmospheric modelling, the relative ratio of TWA concentrations of certain compounds can be even more useful. While absolute concentrations are affected by vertical mixing and other atmospheric processes, the relative ratios are solely dependent on differences in the mechanism and rates of photochemical reactions provided that the compounds are emitted from the same sources at nearly constant emission ratio. Aromatic hydrocarbons are ideal candidates for such studies, as they are reactive in the atmosphere, have life times of several hours and, in addition, they can be diffusively sampled. Two of the most abundant aromatic hydrocarbons, toluene and xylenes, are especially worth studying, as there are quite significant differences between their reactivity (toluene is five times and xylenes nineteen times as reactive as benzene in their reactions with OH radicals [5–8]). In this study the relative concentration ratio of toluene and xylenes was used to determine the similarity as “distance” of the sampling site from traffic-originated emission sources, assuming that transport was the predominant source of these compounds. This is a problem of topical interest since for NMHCs the conventional distinction between “urban”, “industrial” and “rural” sites can hardly be supported any longer: the traffic accounting for 70% of the emissions cannot be localized to the downtown of the cities as a dense network of busy highways covers the countryside [9].

An area located in the proximity of the Italian Highway A1, and characterized by intensive farming as well as some petrochemical activity were investigated, in order to study the relationship between the distance from the highway and to aid the selection of an effective strategy for maintain a good indoor air quality.

2 Site description

The area selected for the measurements, located near Highway A1, close to the Italian town of Lodi, is characterised by a flat ground and the presence of a number of dairies and feedlots. Schematic representation of the area and sites chosen for measurements are shown in Figures 1 and 2. The traffic flow on the highway was estimated by counting the numbers of cars and heavy trucks passing by in a random 5 min periods during the daily measurements. The diurnal average traffic densities during the measurements were 2500-5000 vehicles per hour, around 35% of which were trucks.

3 Experimental results and discussion

Measurements were made at distances of 10 m, 30 m, 70 m, 750 m, respectively from the fence of the highway. Figure 2 shows the sampling layout. The closest point to the source (at 10 m) was used as a reference point. Air samples, contaminated by traffic and possibly by other sources of emissions, were collected by means of an active and passive sampling. *Radiello*$^{@}$ axial diffusive tubes filled with Carbotrap-B and with a solid sorbent doped with Triethanolamine were continuously exposed for ten to fifteen days. VOC were analysed in the laboratory using gas chromatography (column type: Ultra1 30m x 0.32 mm x 0.52 μm) + FID. Main inorganic ions were collected by extraction with deionised water and analysed by liquid chromatography.

In Figure 3 the concentrations of NO_2, representative of summer and autumn time intervals, are plotted against the logarithm of the distance from highway. The measurements show a strong correlation between the NO_2 concentration, C(x), and the logarithm of the distance in metres from the highway. The following model was assumed to apply in the vicinity of the road: $C(x)=C_b+C_0-k*Log(x)$, where C(x) is the concentration at distance x (m) from the highway, C_b is the general background concentration of NO_2, C_0 is the concentration contributed by the high road at x = 0 and k is a constant. A point 10 m far from the highroad, was used as the highway source emission and used as reference point to calculate relative site concentrations as $C_{rel}=(C_x-C_b)/C_{ref}$. This transformation is introduced to obtain a relationship between the relative concentration and the logarithm of the distance from the highroad: $C_{(rel)} = (C_0-K*Log(x))*1/C_{ref}$. The resulting regressions compared in Figure 4, show that the slope obtained during summer and autumn typical whether conditions are similar but somewhat steeper than that reported in literature. Hence the indications from the present study substantially support the result obtained by Gilbert et al. [1] that the NO_2 concentration nearby a highway can be assumed to vary linearly with the logarithm of the distance from the highway. The slope of the regression

line has been previously related to differences in the roughness of the landscape, wind speed and atmospheric stability. However the agricultural landscape characterizing the location under investigation had a very low-roughness, not likely to explain the steeper gradient and also the more stable atmospheric stability characterizing autumn whether can not be called to account for. A different approach, based on a toluene-xylenes ratio as a tool to characterize the local emission sources was then considered. First, the relative toluene to xylenes concentration ratio, expressed in $\mu g/m^3$, was determined at the reference site (herein after referred to as "highway emission ratio") using TWA concentrations (ten to fifteen days sampling time) to minimize the effects of changes due to local factors. The ratio of the TWA concentrations of these compounds was also measured at different sampling sites (hereinafter referred to as "site ratio"). Knowing these values, the rate constants and mechanism of predominant photochemical processes, it is then possible to calculate the time required for the transformation of the source emission ratio into the site ratio. The parameter thus obtained can also be used to characterize a "distance" of the sampling site from traffic-originated emission sources.

4 Degradation mechanisms for toluene and xylenes

Toluene and xylenes, as monoaromatic hydrocarbons react very slowly with ozone and NO_3 radicals, their rate constants being of the order of $<10^{-20}$ and $<10^{-16}$ cm^3 *$molecule^{-1}s^{-1}$, respectively. Thus their depletion in the atmosphere via these reactions is negligible. The only significant process for the atmospheric loss of these compounds is their photochemical reaction with OH radicals, having rate constants $5.96*10^{-12}$ and $2.36*10^{-11}$ cm^3*$molecule^{-1}s^{-1}$ for toluene and xylenes, respectively.

The average daily concentration of OH radicals on the northern hemisphere at mid-latitudes, near ground level, according to a recent study, is $2*10^6$ molecule*cm^{-3} during summer and $0.8*10^6$ molecule*cm^{-3} during autumn [9]. Having determined the "highway emission ratio", subsequent calculations can be performed: the concentration of toluene is reduced by the reaction with OH radicals as well as by air mixing.

If C(s) is the time-weighted average concentration of toluene and xylenes respectively at the sampling site in $\mu g/m^3$, C(e) the time-weighted average concentration as determined in the reference site,

$$C(i_s) = f(t) \cdot C(i_e) \cdot e^{K(i) \cdot C(OH) \cdot t} \quad (1)$$

where $f(t)$ is the time-dependent mixing factor, $K(i)$ is the rate of reaction of the compound (i) with OH radicals, $C(OH)$ is the average daylight concentration of OH radicals at the sampling site during the sampling period in molecule/cm^3, and t the time in seconds. Introducing the terms $C_{Toluene}/C_{Xylenes}$, "r_s , site ratio" and "r_e , reference highway emission ratio", $r_{S=} C_{(T)}/C_{(X)}$, at the site ratio, and $r_e = C_{(T)}/C_{(X)}$, at the source emission ratio can be obtained.

Finally, expression of

$$t = \frac{\ln(r_s / r_e)}{(k_x - k_t) \cdot C(OH)} \quad (2)$$

yields the time *t*, which may be termed the "traffic-equivalent distance". On the basis of the above calculations, the traffic-equivalent distance may be defined as the number of daylight hours required to convert the source emission ratio into the site ratio assuming steady-state OH radical concentration. This parameter may be used to characterize the "distance" of the sampling site from traffic-originated emission sources. The values obtained are reported on Figures 5 and 6 and summarized in Tables 1 and 2.

Table 1: Site distance from the highway, TWA concentrations of toluene and xylenes, calculated site ratio and calculated source equivalent distances (in hours) during summer atmospheric conditions.

Site (distance m)	$C_{Toluene}$ $\mu g/m^3$	$C_{Xylenes}$ $\mu g/m^3$	Site ratio C(T)/C(X)	Traffic equivalent distance (h)
1 (10)	36	24	1.50	0
2 (30)	31	16	1.95	2.07
3 (70)	28	13	2.15	2.93
4 (750)	21	9	2.33	3.57

Table 2: Site distance from the highway, TWA concentrations of toluene and xylenes, calculated site ratio and calculated source equivalent distances (in hours) during autumn atmospheric conditions.

Site (distance m)	$C_{Toluene}$ $\mu g/m^3$	$C_{Xylenes}$ $\mu g/m^3$	Site ratio C(T)/C(X)	Traffic equivalent distance (h)
1 (10)	6	3.3	1.8	0
2 (30)	5	2.5	2.0	2.77
3 (70)	4	1.9	2.1	4.05
4 (750)	3	1.6	1.9	1.42

As can be seen from the data of Table 1, in summer, the absolute concentrations of toluene decrease when moving from the highway location (Site 1) to less polluted background areas (Site 4). If, however, the concentrations of xylenes are compared, the decrease is much more pronounced. However, the absolute concentrations are largely dependent on many factors which are not possible to account, hence their site ratio was considered. The value of 1.50 characterizing the Site 1 is close to that found for urban locations

(1.36 s.d 0.37 for 7 roadside urban microenvironments sites), while this parameter for remote areas is close to one [10–12]. The difference found in the background rural area (Site 4, ratio 2.33), suggests that in the area others sources of aromatic hydrocarbons do exist (as is typical for a refinery or a chemical cracking plant), and their contribution are superimposed upon the traffic emissions.

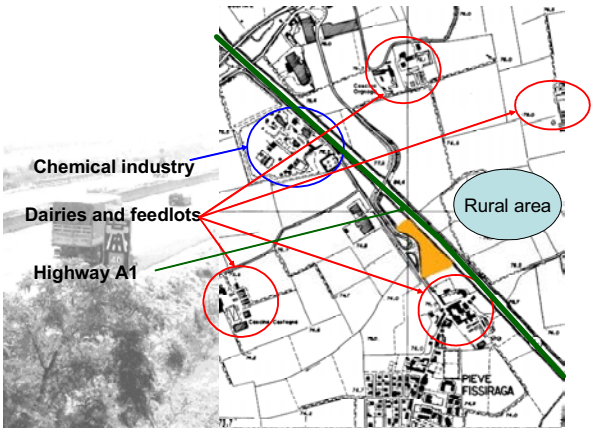

Figure 1: Spatial site characteristics.

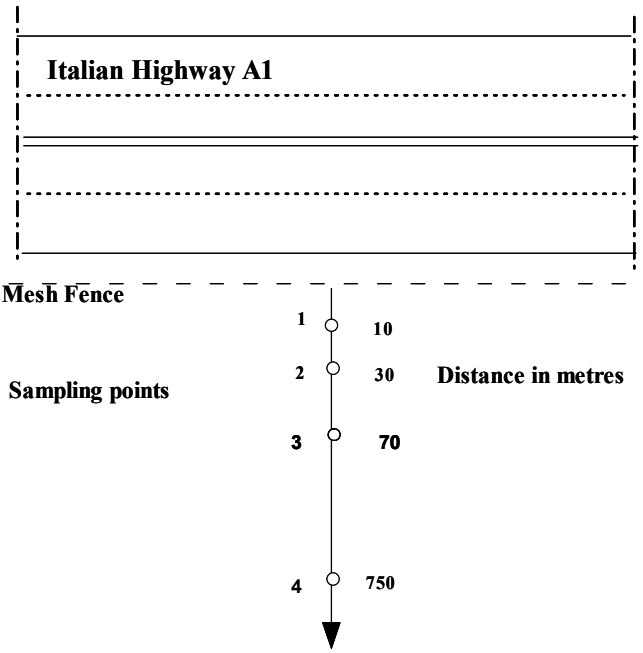

Figure 2: Distance from the road and the sampling points (metres).

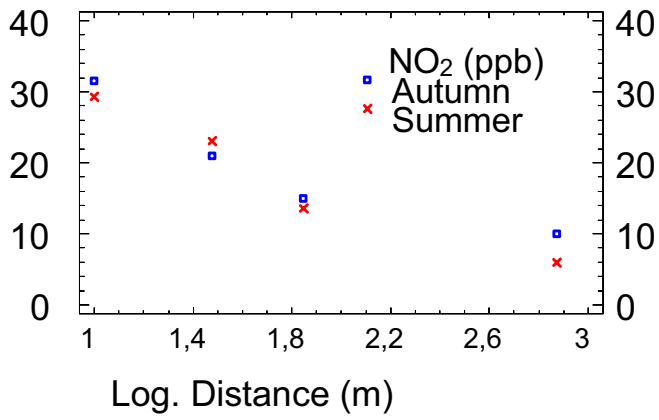

Figure 3: Relationship between concentration of NO_2 (Cx, ppb) and the logarithm of the distance (m) from the highway.

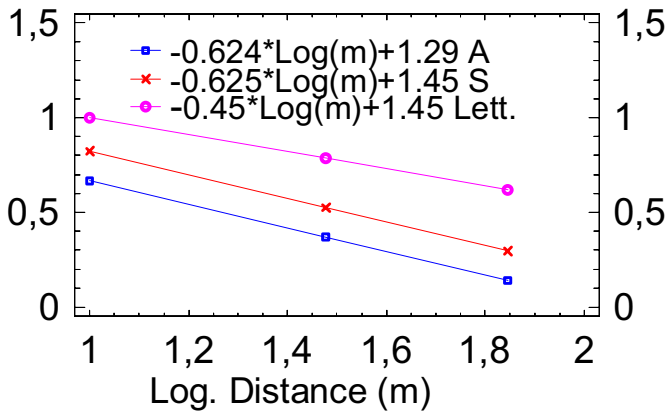

Figure 4: Relationships between the relative concentration (Crel) and the logarithm of the distance (m) from the highway.

The difference is also manifest for the traffic-equivalent distance (TED). Assuming the highway as the emission source, the time distance becomes higher with the distance from the highway (Tables 1 and 2). Interesting appears the autumn situation, when, while the concentrations are significantly lower than those found in summer, the calculated site ratio and traffic-equivalent distance (2-4 h) are similar except for the more distant site (750 m) (Figure 6). These results point out that the distance of the emission sources does not change, but their intensity does. Only in the autumn at the Site 4, both the toluene/xylene site

ratio and TED appear changed again implying that local additional sources, different from traffic must be accounted for.

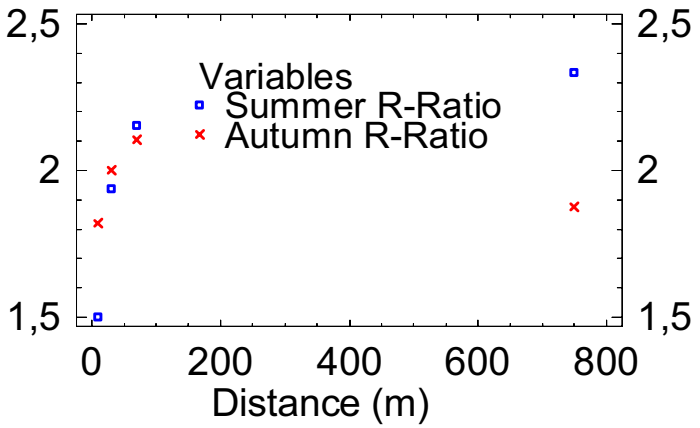

Figure 5: Calculated site ratio for toluene and xylenes during summer and autumn atmospheric conditions.

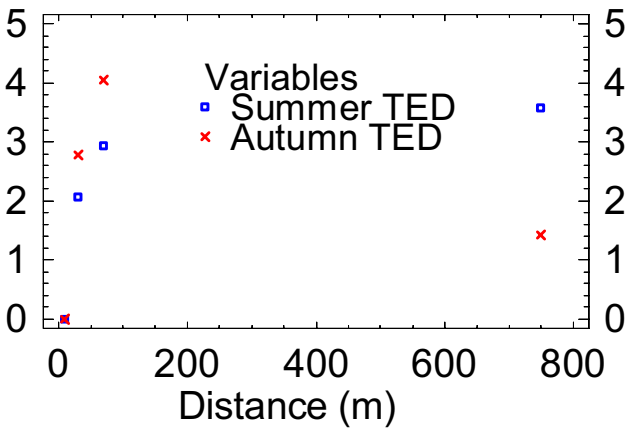

Figure 6: Calculated traffic-equivalent distance (h) for summer and autumn conditions.

5 Conclusions

The purposes of this study were to evaluate the applicability of a traffic emission reference based on NO_2 gradient and to apply the proposed method to assess traffic contribution to individual hydrocarbons in a rural agricultural area

characterized by the presence of a busy highway. The present study confirmed that NO_2 concentration nearby a highway varies linearly with the logarithm of the distance from the highway, but the slope found for this regression was somewhat steeper than those reported in the literature for urban conditions. The relationship between NO_2 concentration and the distance from the highway cannot be assumed to be representative of more unreactive species in traffic exhausts, but can be an useful index for certain types of technological deployment as building ventilation and indoor air quality evaluation. In accordance with literature, the results of the present investigation point to a downwind distance of about 300 m to eliminate measurable influence of a highway on the NO_2 concentration. The average concentrations of VOCs like toluene and xylenes in the study area were similar to those measured in urban areas without major industrial sources. This finding was somewhat unexpected because the study area was not affected by general urban emissions being a typical agricultural area. The results show that some chemical species, such as toluene or xylenes, are emitted from non-traffic sources and were significant during the two sampling periods. By comparing the toluene/xylenes ratios observed in the area with traffic reference values, one can quickly diagnose the significance of non-traffic emissions lending to the selection on an effective control technology and planning to enhance indoor air quality.

It can then be concluded that the site ratio and traffic-equivalent distance parameters are more useful for the characterization of a given site with respect to the proximity of vehicular emission sources than the absolute concentrations of some selected pollutants.

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Section 4
Emission studies

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Decreasing greenhouse effect in agriculture using biodiesel – when green may be enough

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Abstract

In the last decade a great number of studies have been carried out on the possible use of biofuels in order to reduce greenhouse gas emissions. Among biofuels, biodiesel has gained considerable attention as the need to develop alternatives to traditional diesel fuel increases. The Italian parliament adopted directive 2003/30/CE from the European Parliament, in which the guidelines about future production and consumption of biofuels are reported: 1% and 2.5% of biofuels within 2005 and 2010 respectively. The aim of this work is to investigate the reduction in greenhouse gas emission obtained by using biodiesel in agricultural practises, and the role of renewable energy use at a local scale. Comparison between diesel and sunflower methyl ester was made from the point of view of an emission inventory, from production and combustion, by using different scientific tools, such as IPCC methodology and the Danish Life Cycle Assessment (LCA) EDIP Database. Results show that the use of sunflower methyl ester, other than the renewability of CO_2 emitted, implies a general reduction of CO_2 equivalent emissions of up to 57%.
Keywords: biodiesel, sunflower, renewability, GHG, catalysts, CO_2 equivalent.

1 Introduction

In this paper we address the increasing need for environmental safeguards concerning the production of energy. Fossil fuels used every day are not environmental friendly. Therefore, we arrive at the question: "is it possible to produce fuels for antrophic needs and respect the environment?" From this point of view biofuels could bring ecological advantages with good energy efficiency and a certain degree of sustainability [2]. Among biofuels, biodiesel, a fuel that

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can be made from renewable biological sources such as vegetable oils or animal fats, has been recognized as an alternative fuel to substitute conventional fuel, for diesel engines. From an ecological point of view there is ecotoxicological evidence about the properties of biodiesel, like the low resistance to microorganisms biodegradation and biotransformation with respect to fossil diesel as reported by other studies [3, 4]. Biodiesel is produced by using crop productions like rapeseed, soy, sunflower, but also from some species of marine algae [5, 6,]. Although the first diesel cycle engine invented by Rudolf Diesel ran on peanut oil [7], with the increase of fossil fuels production, conventional diesel became the only fuel used. The consumption of 3.8×10^{12} kg per year of fossil fuels [8], developed great influence on atmospheric dynamics and global climate change. About 2.54×10^{13} kg of CO_2 are added to the atmosphere annually [9]. At the moment it is impossible to substitute diesel fuel with biodiesel absolutely. However, there is the possibility of using biodiesel in the agriculture compartment in order to reduce green house gases emission, and moreover to reduce the agricultural industries' dependence on fossil energy. The aim of this study is to demonstrate, by using pure biodiesel (BD 100), the possible emissions and land use scenarios from a simulation of a farm system of Siena province, Italy.

2 Methods

We tested the effective reduction in green house gases emissions, using biodiesel fuel from sunflower cultivation, from its oil seed transesterification, and from its final combustion. We will also evaluate the level of sustainability of the entire process, from the point of view of land requirement and the renewability of CO_2 emissions. The inventory of emission refers to the following gases: Carbon dioxide (CO_2), Nitrous oxide (N_2O), Methane (CH_4).

The simulation shows three possible steps; each of them has its own weight in emissions dynamics.

- *Step a*, in which we start to quantify the fossil diesel used and the related emissions in a typical Tuscan farm for wine production; here we have selected a representative farm system;.
- *Step b* in which we calculate the amount of biodiesel production required (agricultural phase) to replace fossil diesel: the land use for sunflower production, fossil fuel required and related emissions. Here we have selected a typical farm system (1000 ha) for sunflower cultivation.
- *Step c* in which we consider the farm system self sufficient for wine and biodiesel production, using biodiesel fuel only, (agricultural and industrial phase) and related emissions.

Our simulations are based on different data set:

- diesel fuel quantities for wine and sunflower production are obtained from field data collection, in which the diesel fuel consumption for each field operation is reported;

- emissions of diesel fuel production are based on data obtained from the Danish Life Cycle Assessment (LCA) EDIP Database [10];
- emissions of diesel fuel combustion are calculated by using IPCC methodology-module Energy [11];
- emissions of biodiesel agricultural production are calculated by using IPCC methodology-module Agriculture [11];
- emissions of biodiesel industrial production are calculated by using data from the EU Biofit project [12];
- emissions of biodiesel combustion are calculated from the results of the EPA Biodiesel Emissions Database [13].

3 Results

3.1 Step a.

As mentioned previously, the first step is to investigate diesel fuel consumption in a local vineyard. Data collected refers to a consumption estimated at 658 kg ha^{-1} $year^{-1}$ for field operations. First of all we have calculated emissions from diesel fuel production. We used data from the Danish Life Cycle Assessment (LCA) EDIP Database, in which all raw material input for each operation and related gas emission output for each 1 kg of diesel fuel produced is reported. The second step was to calculate emissions from diesel fuel combustion, using IPCC methodology, Module 1 Energy. In Table 1 the emissions related to the total diesel fuel quantities used in the vineyard. By multiplying this result for Global Warming Potential (GWP) of methane and nitrous oxide we obtained the total CO_2 equivalent emissions (Table 2).

Table 1: Emissions from total diesel fuel consumption (658 kg).

	Diesel production	**Diesel combustion**	**Total diesel use**
CO_2	3.02E+02	2.09E+03	2.39E+03
CH_4	2.82E+00	1.43E-01	2.96E+00
N_2O	7.63E-03	1.71E-02	2.47E-02

Table 2: Total carbon dioxide (CO2) emissions (kg) from diesel use.

GHG	**GWP**	**CO_2 equivalent**
CO_2	1	2.39E+03
CH_4	21	6.82E+01
N_2O	310	7.32E+00
Total CO_2 equivalent		2.47E+03

3.2 Step b.

Before illustrating step b we have to introduce a new parameter to calculate the amount of biodiesel production that depends on sunflower oil-seed yield. Emissions from the "biodiesel system" depend on the amount of land used for its production; from this point of view the higher the industrial transformation yield, the lower land use and related emissions. To remark this concept for our simulation, we refer to the study conduced by Vicente *et al*. [14] in which a comparison is made between different basic catalysts for methanolysis of sunflower oil, in transesterification process. The catalysts are sodium hydroxide, potassium hydroxide, sodium methoxide, potassium methoxide and each catalyst has a specific biodiesel yield (wt%) in the transformation process as follows: 86.71%, 91.67%, 99.33%, 98.46%, respectively. The amount of biodiesel necessary to substitute diesel used for vineyard field operations was calculated by using the comparison of the net calorific value of the two fuels; since biodiesel has lower net calorific value than diesel, 756 kg of biodiesel was required to replace 658 kg of diesel. According to previous methodology explications, data about diesel consumption necessary to sunflower cultivation came from a 1000 ha area of cultivated farmland, and the sum of all diesel consumptions of field operations is 108 kg. From field data and statistical data collected [15], sunflower seed yield was estimated to vary between 1500 and 2500 kg ha^{-1}; Kallivroussis *et al.* [16] reports the yield of raw oil output from the seed crushing process is fixed at 32-38%. To calculate the yield of biodiesel we assumed a value of 2000 kg of sunflower seeds with a yield in the transesterification process fixed in 35% (Table 3). Another important variable is the fertilizer input necessary for sunflower cultivation. From field data we reported the quantity of nitrogen fertilizer to be fixed at 200 kg ha^{1}. At this point we were able to calculate the amount of land use, fertilizer input, diesel fuel consumption, all related to the yield of different catalysts used, and related emissions. In Table 4 we reported land use, fertilizer and diesel consumption necessary to biodiesel production referred to two fixed values, sunflower seed yield, and oilseed yield, 2000 kg and 35% respectively.

Table 3: Biodiesel yield, kg ha^{-1} related to different catalysts.

Sodium hydroxide	Potassium hydroxide	Potassium methoxide	Sodium methoxide
606.97	641.69	689.22	695.31

Table 4: Land use (ha), fertilizer (kg) and diesel consumption (kg) necessary to biodiesel production.

Catalysts	Land use (ha)	N fertilizers (kg)	Diesel (kg)
Sodium hydroxide	1.45E+00	2.90E+02	1.56E+02
Potassium hydroxide	1.37E+00	2.74E+02	1.48E+02
Potassium methoxide	1.28E+00	2.55E+02	1.38E+02
Sodium methoxide	1.27E+00	2.53E+02	1.37E+02

In Table 5 emission gases related to aggregate quantities of diesel fuel used for wine and sunflower production are reported. Emissions are accounted for total diesel quantity production and combustion; diesel quantity for sunflower cultivation will be lower when the catalyst's yield is high, because of the lower land use.

Table 5: Emission gases (kg) from aggregate diesel fuel quantities for wine and sunflower production; N_2O^{f} refers to nitrous oxide from fertilizers used for sunflower cultivation, N_2O^{c} refers to nitrous oxide from diesel fuel.

	S. hydroxide	P. hydroxide	P. methoxide	S. methoxyde
CO_2	2.961E+03	2.930E+03	2.893E+03	2.889E+03
CH_4	3.670E+00	3.632E+00	3.586E+00	3.580E+00
N_2O^{f}	3.279E+00	3.102E+00	2.888E+00	2.863E+00
N_2O^{c}	3.062E-02	3.030E-02	2.991E-02	2.987E-02

3.3 Step c.

In this phase of our simulation we start from the assumption that the farm system is self sufficient, for wine and sunflower production, by using only biodiesel. In this case all emissions will be related to biodiesel production and combustion. Biodiesel production is divided into two phases:

- agricultural phase, in which the input considered are land use (ha), nitrogen fertilizers (kg ha^{-1}), and their emissions;
- industrial phase, in which we consider all raw materials and processes and related emissions that refer to biodiesel quantity produced;
- combustion refers to all field operations (wine and sunflower production).

The biodiesel quantity necessary for 1 ha of wine and sunflower production has been calculated to be 880 kg; in Table 6 we report land use, N fertilizer quantity and related emissions as N_2O.

Table 6: Land use, N fertilizer quantity and related emissions as N_2O.

Catalysts	Land use (ha)	N fertilizer (kg)	N_2O emissions (kg)
Sodium hydroxide	1.45E+00	2.90E+02	3.279E+00
Potassium hydroxide	1.37E+00	2.74E+02	3.102E+00
Potassium methoxide	1.28E+00	2.55E+02	2.888E+00
Sodyum methoxyde	1.27E+00	2.53E+02	2.863E+00

Biodiesel industrial production refers to the transesterification process in which sunflower oil seeds are transformed in methylester and other by-products like glycerine, using catalysts for chemical reactions. Calculations for greenhouse gas emissions are based on the EU Biofit 2000 project, in which

eight European countries and related research institutes (BLT, Austria; TUD, Denmark; INRA, France; IFEU, Germany; CRES, Greece; CTI, Italy; CLM, The Netherlands; FAT, Switzerland) analyzed production and use of biofuels, with an LCA methodology that take in account all emissions (g of gases $tons^{-1}$ of biodiesel). So we report our calculations for this phase in Table 7.

Table 7: Emission (kg) from industrial phase for 880 kg biodiesel transesterification.

CO_2	CH_4	N_2O
2.04E+02	1.70E+00	8.36E-02

The last aspects of this step are biodiesel emissions from combustion. Calculations are based on EPA Biodiesel Emissions Database, in which the emission test cycle using different blends of methylester (biodiesel) in different engine types is reported; we selected data referred to pure biodiesel (BD100) and values used in our calculations come out from an average of different tests. Emissions tested by EPA considered CO_2, CO, NO_x and THC. THC refers to total hydrocarbons, in which CH_4 is included. In Table 8 we show first emissions from biodiesel combustion related to sunflower field operations; BD100 quantities and emissions decrease with the increase of catalysts yield, because of the reduction of land use.

Table 8: Emissions (kg) from biodiesel (BD100) combustion for sunflower field operations.

Catalysts	Biodiesel (kg)	CO_2	THC	CO	NO_x
S. hydroxide	1.80E+02	4.82E+02	7.60E-02	1.00E+00	4.86E+00
P. hydroxide	1.70E+02	4.55E+02	7.10E-02	9.60E-01	4.59E+00
P. methoxide	1.58E+02	4.22E+02	6.60E-02	8.90E-01	4.27E+00
S. methoxide	1.57E+02	4.20E+02	6.58E-02	8.80E-01	4.24E+00

Second we report, in Table 9, biodiesel emissions from wine production.

Table 9: Emissions from biodiesel (BD100) combustion for wine yard field operations.

Biodiesel (kg)	CO_2	THC	CO	NO_x
7.56E+02	2.20E+03	3.17E-02	4.28E+00	2.04E+01

4 Discussion

In order to explain what are the emission trends from a point of view of emissions at local scale, for vineyard system we summarized the trend of CO_2 equivalent emissions (CO_2, CH_4, N_2O) in Fig. 1; at t0, in which there is only diesel fuel production and consumption emissions, shows a value of 2.47+03 kg;

at t1, in which the diesel production and consumption for wine and sunflower production is considered, the value increases until 3.95+03 kg; at t2, in which only biodiesel is used for all field operations, the value has a little lessening until 3.69+03 kg (biodiesel production an consumption). In t2-CO_2 renew, there is the removal of CO_2 emissions considered renewable; the difference in petroleum diesel and biodiesel is the time of carbon dioxide fixation; in the case of fossil diesel the process occurred in geological time, while for biodiesel carbon dioxide released in atmosphere is fixed in recent years [17, 18] and sunflower cultivation uses it every year. Following this assumption if we remove CO_2 emissions from biodiesel combustion, we have a value of 1.05+03 kg.

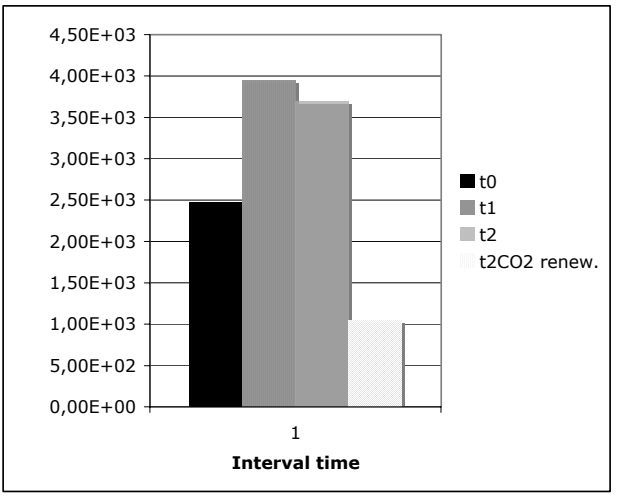

Figure 1: CO_2 equivalent emissions for vineyard system.

So the reduction between t0 and t2-CO_2renew for vineyard system is about 57%. The potential of CO_2 equivalent reduction for biodiesel production is reported in some works; in 'Evaluation of the comparative energy, global warming and socio-economic costs and benefit of biodiesel', by the Sheffield Hallam University [19], we found a comparison between diesel and biodiesel production; the reduction GHG emission ($kgCO_2eq/kgbiodiesel$) for biodiesel is about -61%. In 'Life cycle inventory of biodiesel and petroleum diesel for use in urban bus' (1998), by the National Renewable Energy Laboratory [20], we found that the life cycle emissions of CO_2, on 100% biodiesel, are 78% lower than those of petroleum diesel, and this reduction is linked to the carbon recycling by soy cultivation. Emissions from fossil diesel combustion in are calculated using IPCC methodology, module 1 Energy, and emissions from nitrogen fertilizer (N_2O) using module 4 Agriculture. We are aware that some authors [21] show that in some conditions the default value used to calculate emissions are not representative, and they can underestimate or overestimate relative emissions values. We are sure that for specific processes at local scale, an appropriate

approach could be found; however, IPCC methodology is widely used and the only one scientifically accepted, even if it needs improvement.

5 Conclusion

There are a large number of comparative studies on the possibilities for diesel and biodiesel use. Our simulation study confirms that biodiesel (BD100) production (agricultural an industrial phases) and combustion are climate friendly. A 57% reduction in CO_2 equivalent emission is possible by using BD100, owing to the renewability of CO_2 from its combustion fixed by the growing biomass (sunflower). At scale of Province, emissions reduction comes out from a system self-sufficient from a point of view of fossil fuels use. The results could be lower if farm systems conduction approached to organic farm conduction.

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Trends and sources identification of non-methane hydrocarbons (NMHC) concentration in rural areas in France

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Abstract

Investigations on long term trends of non-methane hydrocarbons (NMHCs) in rural areas are of interest for a better understanding of tropospheric ozone concentration. NMHC were measured on a French rural site from 2002 to 2005, as part of the EMEP program. First, the examination of the levels and trends showed a global decrease in NMHCs. These results are in accordance with the levels observed in other sites in Europe. They are also in agreement with the decrease of NMHC emissions in France as positive consequences of the European directive 99/13/CE. Nevertheless, we note a pronounced increase in biogenic compounds like isoprene, one species having a high potential of ozone formation. Secondly, data handling was based on receptor modelling using Positive Matrix Factorization (PMF) to characterize NMHC source profiles and their contributions. Six main profiles have been identified: domestic heating (28.2%); remote sources (22.1%), solvent use (18.4%), vehicle exhaust (10.6%), gasoline evaporation (9.9%) and biogenic (7.1%). This work is completed by a clustering analysis of air trajectories in order to apportion local and regional source contributions to the measured concentrations on the sampling site. The final aim of this study is to carry out a NMHC data extensive analysis in order to improve the comprehension of the increase trend of background ozone.
Keywords: NMHC, rural atmosphere, trajectory analysis, receptor model, PMF, source apportionment.

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1 Introduction

It has been well established that non methane hydrocarbons (NMHC) play an important role as precursors to ozone and other secondary photochemical pollutants. Ozone exceedences continue to be a major problem, especially at rural location in Europe where a large fraction (10-40%) of the population, was exposed to ground-level ozone concentrations above the health-protection-based target level [14]. For that reason, the relationship between ozone and its precursors still remains an issue of important concern. The distribution of NMHC is the result of three major combined processes: (1) primary and secondary formation process, (2) removal process and (3) mixing process.

(1) Sources and primary NMHC are both of anthropogenic and biogenic origin. Major anthropogenic sources are related to fossil fuel combustion (vehicle exhaust, heat generation, combustion in industries), storage and distribution of fuel (evaporation) and solvent use [7].
(2) Mechanisms of NMHC oxidations are mainly induced by the hydroxyl radical OH in daytime, by the NO_3 at night, and ozonolysis for unsatured compounds [1].
(3) Mixing process, closely related to meteorological conditions within the mixing boundary layer, tend to redistribute the pollutants through advective and convective transport at a regional or long-range scale, especially for long life time species (ethane, propane).

The consideration of the relative importance of these factors can provide relevant information for a better understanding on NMHC impact on tropospheric chemistry. The objective of this work is to assess and apportion sources of rural NMHC on a temporal basis. To do so, a receptor model approach was used to analyse data of one rural site in France.

2 Sampling site and measurement methods

2.1 Sites description

Data sets (N=390, completeness=93.5%) used in this study correspond to samples collected at one of the three rural EMEP sites of Tardière belonging to the French rural monitoring network called MERA (MEsure des Retombées Atmosphériques). The site (Figure 1) is located 1 km in the north of a small urban area (3,000 ha) and 50 km away from the sea. The most polluted area is located 100 km in the northeast of the site with a big urban centre (Nantes 270,000 ha.) and a petroleum refining plant.

2.2 NMHC sampling and analysis

Measurements have been performed since 2002. Sampling is carried out twice a week on Tuesdays and Thursdays around 12:00 UT for 4 hours.

Stainless steel canisters (6L) provide the collection of NMHC samples according to the well-established TO-14 method [21] for many none polar VOC,

so used in the EMEP network. NMHC sampling has been done with canister sampler from Andersen instruments Inc. NMHC analysis is carried out by a VOC analyser (VOCAA from Chrompack equipped by an auto TCT/CP9000-GC). Separation is performed by a dual capillary column system equipped with a switching device. The analytical conditions were described by Locoge and Galloo [16]. Four main steps constitute the QA/QC programme which is based on the TO-14 method (1997): (1) the establishment of standard operating procedures, (2) canister cleaning and certification (<0.02ppbv), (3) sampling system cleaning and lab certification, (4) in-situ tests with collocated samplers in field.

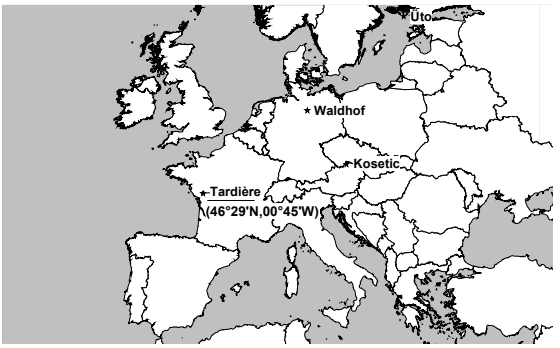

Figure 1: The Tardière sampling site and other EMEP sites.

3 Levels and trends

The annual average concentrations reported in table 1 are in good agreement with those observed in the other EMEP sites (http://www.nilu.no/projects/ccc/emepdata). That confirms the rural typology of this site. Besides, French site denotes by its higher concentrations in isoprene due to its climatology and the density of its vegetation.

Table 1: Comparison with other EMEP sites located in Figure 1 (Annual average in ppb).

	Ethane				Acetylene				Isoprene			
Site	2002	2003	2004	2005	2002	2003	2004	2005	2002	2003	2004	2005
Tardière (France)	1.794	1.864	1.785	1.732	0.446	0.546	0.477	0.439	0.119	0.190	0.150	0.157
Úto (Finland)	1.692	2.012	1.611		0.336	0.449	0.362		0.017			
Waldhof (Germany)	1.784	1.824	1.760		0.707	0.824	0.789		0.031	0.033	0.04	
Kosetic (Czech Republic)	2.189	1.994	1.641		1.136	0.97	0.819		0.041	0.047	0.026	

As already observed in rural and remote sites [9, 20], NMHC exhibit pronounced seasonal cycles (Figure 2). The cycle of anthropogenic compounds (e.g. ethane, acetylene and benzene) shows maxima in winter which reflects emission strengthening in that period, for instance with heating function and

vehicle "cold start" effect. In addition, chemical lifetimes of hydrocarbons are prolonged due to the low concentration of OH and the weaker UV-radiation compared to in summer. Furthermore, the height of the mixed boundary layer is often lower in winter than in summer. Moreover, summer minima highlights photochemical process. For C_2-C_4 alkanes, ground levels persist due to their long atmospheric residence time (several days). For short lived species (few hours), concentrations in summer are sometimes close to the Detection Limits (DL). Isoprene shows a clear opposite cycle indicating the contribution of biogenic emissions in summer. Some very high values occurring in summer for this species are well correlated with high levels of ambient temperature.

Times series (Figure 2) shows systematically some extreme valid values in winter for ethane, acetylene and benzene. Nevertheless, observed concentrations are lower than those observed in urban area. High concentrations of acetylene and benzene are correlated with high levels of short lived species like ethylene or propylene. So these events can be due to combustion emissions (vehicle exhaust or domestic heating) closer to the site. For Ethane, the trajectory analysis confirms that air masses associated with very high values of concentration have passed over urban areas. In the following section, we have considered the sensibility of the model to the extreme values.

Time series (Figure 2) for anthropogenic species have shown decreasing trends especially for benzene in relation to its volume limitation in fuel since 1999 (directive 98/70/EC).

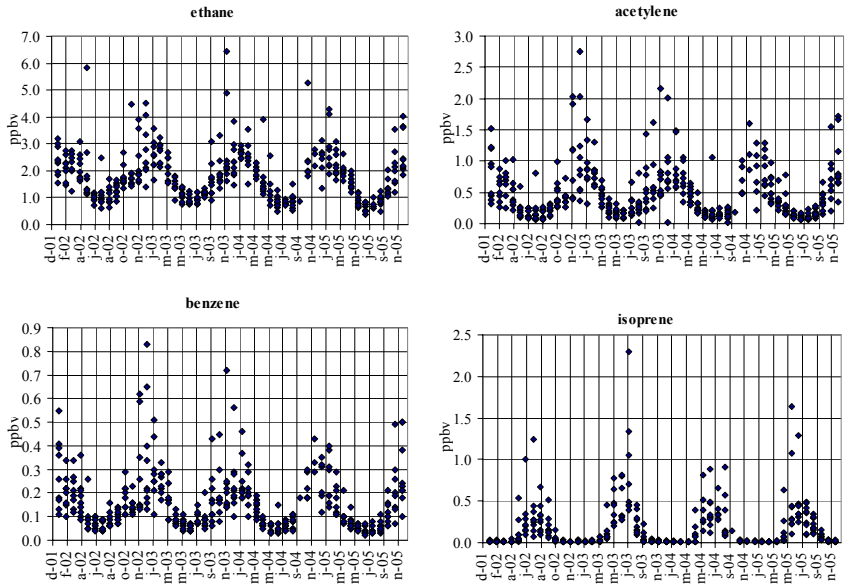

Figure 2: Typical NMHC Time series at Tardière site.

4 Methods

4.1 PMF model

The PMF was described by Paatero and Tapper [18] and has been used in many source identification studies involving VOC measurements in ambient air [2, 15, 23]. The PMF2 program and additional guidance on the use of PMF [13] were used for this study. The PMF2 solve the receptor modelling:

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \tag{1}$$

where x_{ij} is the jth species concentration measured in the ith sample, g_{ik} is the contribution of the kth source to the ith sample, f_{kj} is the jth species mass fraction form the kth source, p is the number of independent sources, and e_{ij} is the residual associated with the concentration of the jth species in the ith sample.

The PMF2 program minimizes the residual sum of squares, Q, given by:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}\frac{e_{ij}^2}{s_{ij}^2} = \sum_{i=1}^{n}\sum_{j=1}^{m}\left(\frac{x_{ij} - \sum_{k=1}^{p} g_{ik} f_{kj}}{s_{ij}}\right)^2 \qquad fkj \geq 0 \text{ and } g_{ik} \geq 0 \tag{2}$$

where s_{ij} is an uncertainty estimate for the jth species measured in the ith sample according to equation:

$$s_{ij} = \sqrt{(DL_i/3)^2 + (0{,}1.x_{ij})^2} \tag{3}$$

DL_i is the detection limit of the analytical method for the ith species. Values below the DL were replaced by half of the DL and 5/6 of DL was assigned as their associated uncertainties [13]. Missing values were replaced by the geometric mean of the measured values, and associated uncertainties were set at four times this geometric mean. Various runs were done in order to optimise the selection of parameters and to test the robustness of PMF model.

Finally, the results were scaled to the measured concentration using a scaling constant, s_k, obtained by regression from the measured NMHC concentrations against the source contributions, g_{ik} :

$$x_{ij} = \sum_{k=1}^{p} (s_k g_{ik})\left(\frac{f_{kj}}{s_k}\right) \tag{4}$$

The number of factors was determined such as (1) additional factors did not improve the Q values significantly, (2) the residual values have a symmetric distribution and were within ± 2, (3) scaling constants s_k from regression were all positive.

The PMF factors were then explained by comparing them with known emission profiles.

4.2 Trajectory analysis

Many studies have demonstrated the influence of atmospheric transport patterns on pollutants concentration by considering air mass trajectories [5,3,4]. Each sample was associated with its 5-day 3-hourly 3D-back trajectories arriving at the sampling station at 12:00 GMT (P=950 hPa). These trajectories were calculated by the British Air Data Centre. K-means clustering algorithm is used to group these trajectories depending on their direction, their speed and their altitude. The aim of this technique is to maximise between-group variance and to minimize within group variance. The method of determining the number of clusters to retain is the same as the one reported in Dorling et al [5].

5 Results and discussion

47 of the 55 measured species were used for PMF analysis. Those with less than 20% of their values above the DL were not considered. Eight factors (reported in Figure 3) were retained for PMF analysis. Good mass reproduction was obtained with this set of factors (R^2 =0.97). Seven of the eight factors have been correctly identified.

The first factor F1 is dominated by ethane, propane, acetylene, butane, benzene and ethylene. Contribution time series shows a marked cycle with maxima in winter. Taking into account the lower urban density (limitation of the number of sources influencing the site), the average winter temperature (8.5°C) and by comparison with emission profiles resulting from GEMENIS database [8], F1 was identified as domestic heating function. This factor represents the highest contribution (28.2%).

Ethane is the predominant compound for factor F6. Because of its low reactivity, it is commonly associated to the contribution of old air masses brought by air transport towards the sampling site or closer sources like natural gas leak. That is the reason why this profile is usually labelled “remote sources” [11.2]. This source shows a significant contribution (22.1%).

Toluene, mp-xylene, o-xylene and ethylbenzene characterize the factor F8 (18.4%). These aromatic compounds are emitted mainly from industrial solvent use sources [10]. The time series since 2002 to 2005 has shown a significant decrease of its contribution.

Ethylene and acetylene are the main components of F2 and F7. These species can be considered as profile of industrial sources or profile of automobile exhaust. Considering the short lifetime of ethylene, and the rural typology of the site without close industrial plant, these factors are associated with vehicle exhaust. The profile of automobile exhaust [6] corroborates this identification. The examination of contributions time series shows that F2 and F7 concern this profile respectively in winter and in summer. These factors represents 10.6% of the total contribution.

The factors F5 are abundant with propane, ethane associated with butane, iso-butane, pentane, iso-pentane, benzene and toluene. This association seems to correspond to evaporative sources like gasoline vapour that usually do not

consist of the combustion compounds or from heavier hydrocarbons that volatilize more slowly [22]. F5 represents a contribution of 9.9%.

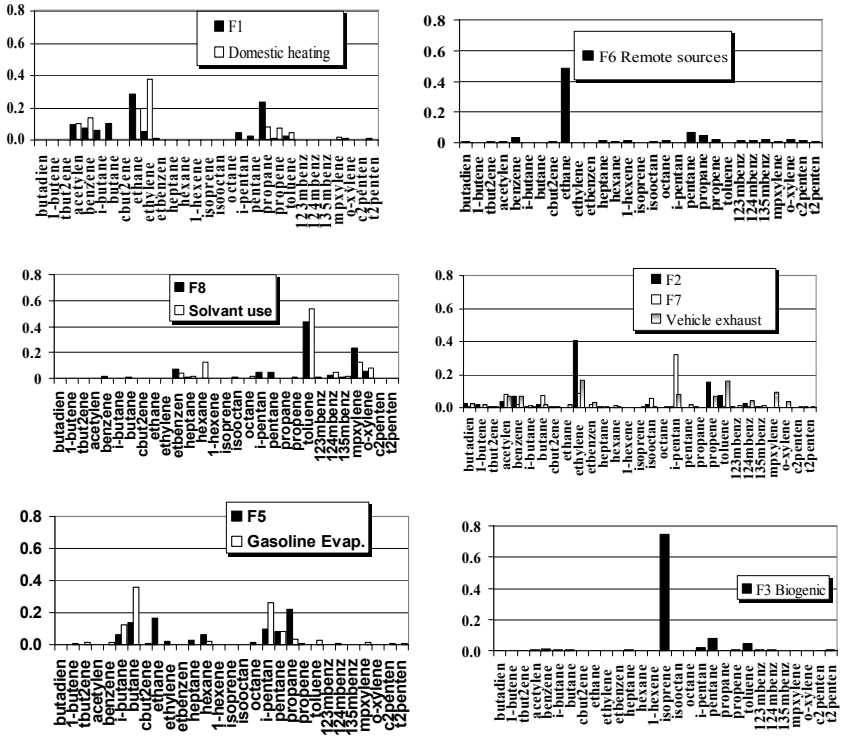

Figure 3: PMF Source factors in comparison with known source profiles.

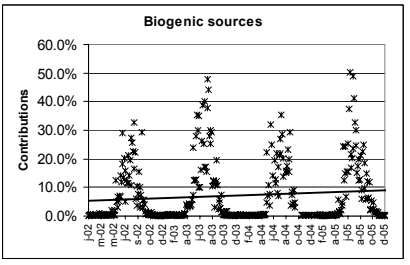

Figure 4: Time series of contribution for biogenic sources

Factor F3 is labelled biogenic emission with isoprene as a predominant compound. Biogenic VOC emissions from vegetation are characterized by isoprene, which is commonly used as the marker of biogenic emissions. This compound is significantly higher in summer (Figure 4) and is well correlated with temperature. A possible contribution of industrial or automobile sources can here be neglected. Moreover, as observed in Figure 4, this moderate

contribution (7.1%) tends to increase which became a particular concern because of the important role of isoprene in ozone formation.

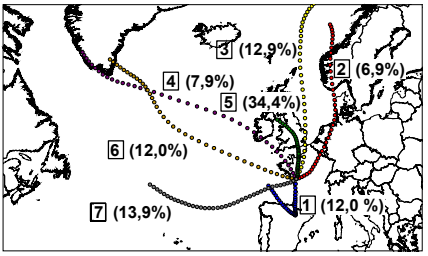

Figure 5: Average trajectories obtained by clustering analysis-relative share (%) of clusters.

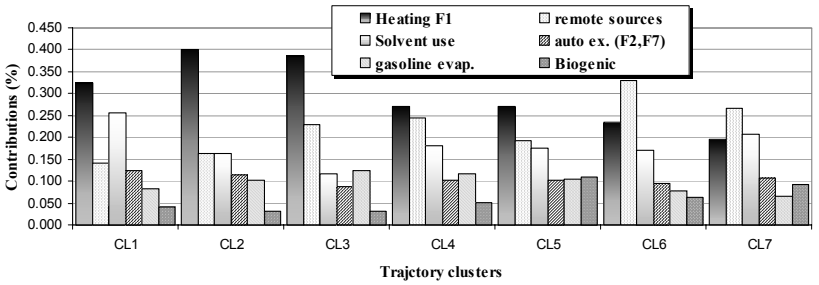

Figure 6: Source contributions.

The average trajectories and the representativeness of the seven clusters obtained are reported in Figure 5. The contributions of factors are reported in Figure 6 for each trajectory cluster. For five by seven clusters, the factor F1 related to heating source remains the principal component. We distinguish one group of clusters (continental clusters 1, 2, 3 and 4) more influenced by local emissions like domestic heating, solvent use or gasoline evaporation exhaust. Besides, Oceanic clusters 6 and 7 are less influenced by nearest urban sources. This group is dominated by the contribution associated with remote sources factor. Cluster 5 is mainly represented in summer. Highest contributions in biogenic sources appear in this cluster in comparison with others.

6 Conclusion

Concentration data of 55 NMHC were measured on a rural site belonging EMEP network. The examination of time series underlines a significant decrease for anthropic compounds especially for Aromatics as positive consequence of European directives. Furthermore, concentrations in isoprene are typically high in France with a significant increasing temporal trend, which is becoming a particular concern due to the important role of isoprene in ozone formation.

Secondly, data handling was analysed by Positive Matrix Factorization PMF to characterize source profiles and to compare their relative importance in rural areas. Six main profiles have been identified: domestic heating (28.2%); remote sources (22.1%), solvent use (18.4%), vehicle exhaust (10.6%), gasoline evaporation (9.9%) and biogenic (7.1%). Resulting from trajectory clustering analysis, the source contributions were shared into two main groups: (1) oceanic characterized by older air masses and (2) continental more influenced by local emissions. In a future work, a backward trajectory method will be applied to source contributions deduced from PMF in order to locate source regions.

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Emission inventory for an urban area: construction and use

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Abstract

The situation of air pollution due to nitrogen oxides in an urban area of North Italy has been evaluated starting from the definition of emission scenario calculated on the basis of specific localisation of emitting sources, their working regime and emission factors. Afterwards, by using specific atmospheric models suitable to the different sources and localisations, it was possible to evaluate the concentration maps; it was also necessary to consider the presence of a stagnating quantity of pollutants forming a background concentration that has been evaluated by means of experimental data. It was possible to ascertain that the traffic contribution, which by itself is quite important from the point of view of the emissive scenario, is the dominant factor as far as the reduction in air quality is concerned. On the basis of this observation, some traffic limitation interventions have been considered, and it was interesting to establish their contribution on air quality. The methodological path that has been constructed presents a numerical significance that is completely site-specific, but it can also be considered a useful tool for the political authority; in fact, on the basis of the correct knowledge of an emissive scenario and a valid atmospheric model, it is possible to set up proper policies for an air quality improvement.
Keywords: traffic, nitrogen oxides, atmospheric model, urban area.

1 Introduction

The air pollution situation of many European urban areas does not present indications of any substantial improvements, in spite of the adoption of technological interventions for emission limitations and processes for source reduction (CAFE Programme, 2005); actually, these actions, without other activities, such as a clear understanding of emissive and atmospheric phenomena

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influencing the result, are not able to lead the air quality back to desired standards.

In order to deal with the problem in the right way, many subsequent elements are necessary, as follows:

- it is necessary to individuate the principal emission fluxes, taking into account the sources spatial distribution and their capacity to generate fixed quantities of pollutants;
- the correlation between emitted fluxes and environmental concentrations must be evaluated by means of atmospheric models, and the results must be compared with experimental values;
- with reference to different emission scenarios, the different effect on air quality must be established, and the obtained concentrations must be evaluated and compared to the required standards; this way, it will be possible to establish criteria for real time limitation or structural interventions.

The above described approach requires, for the first two steps, to overcome some obstacles; with reference to the first task, it is necessary to construct a realistic inventory of emissions produced from different activities, and this inventory must be disaggregated with reference to times and local situations; chiefly for some pollutants (like nitrogen oxides, that will be the subject of this article, while different should be the evaluations about fine dusts) there are not conceptual difficulties for this evaluation, but it is important to underline and stress the attention that must be devoted to collection and organisation of existing technological and territorial data.

In order to study the impact aspects by means of atmospheric models, the influencing mechanisms are completely known and conceptually defined; nevertheless it is necessary to calibrate the models with reference to specific territorial situation, by considering meteorological aspects, spatial and topographic collocation of sources and objects that can hinder the free circulation of air masses; chiefly in urban areas the last one seems to be the most important argument of investigation that must be dealt with. Finally the third step substantially corresponds to an activity of political decision on the basis of verified information and reliable predictions deriving from the individuated scenario; for this step the fundamental role belongs to public authorities, but it must be developed on the ground of solid technical information.

The so defined route will be presented with reference to a city in the North of Italy, where it is strictly necessary to adopt limitation policies; the presence of emissions, meteorological and air quality data is the precondition in order to perform a process of definition and calibration of models, and subsequently to arrive to the definition of improvement scenarios.

The meaning of the described process is highly methodological, as in any territorial situation emission inventories and atmospheric dispersion capacities are different and strongly dependent on the specific area; nevertheless this approach, constructed and calibrated for a specific case, can be usefully extrapolated also to other urban situations.

2 Investigated area, emission and air quality data

The investigated area corresponds to the town of Alba, a middle dimension city (40.000 inhabitants) of North of Italy, where the presence of pollutants (chiefly nitrogen oxides, dusts, ozone) is quite high as a consequence of heavy road traffic, large industrial activities, and domestic heating. The most convenient parameter adopted for the study has been identified in nitrogen oxides, because it represents a critical point in the investigated area, and at the same time one has the possibility of individuating the technological origin of this pollutant. As far as the data that have been used as a basis for the study are concerned, they are as follows.

Meteorological data. From the local Environment Protection Agency it was possible to obtain for a whole solar year (the year 2004 in particular) for two urban stations data about wind direction and wind speed, temperature, solar radiation; these data have been organised with statistic approach as far as the convective component is concerned, while the stability classes have been defined using the SRDT scheme obtained from U.S. EPA; as for the mixing height, with a similar approach, we used screening values provided by U.S. EPA for night or day conditions and different stability classes.

Topographic data. In the main urban streets the traffic fluxes were known, and there the buildings geometry has been evaluated; this way, on the basis of the structure of surrounding buildings, in some cases the geometry has been defined as an urban canyon; otherwise, where the buildings are low, not close to the street or not present, an open spatial structure was considered.

Air quality data. For the year 2004 we have at disposal the measured hourly data of nitrogen oxides concentration in an urban point. The localisation corresponds to a backyard, and so it is possible to consider this series of registrations as representing mean values for the city; as a matter of fact, there is very low influence of local effects, and on the contrary it is possible to identify there an overlapping of the effects of different emitting sources.

Emission data. First of all the contribution deriving from road traffic has been evaluated; the Alba municipality provided hourly values of circulation of different vehicle types for the main streets, and from these values, taking into account the emission factors derived from COPERT III program (Ntziachristos and Samaras [2]) and the length of considered street stretches, it was possible to define linear emissions; when using COPERT III we obviously considered the composition of the vehicle park in different emissive classes, as required from the program. As for the domestic heating, the starting point was the definition of inner volumes where different fuels (natural gas, gas oil, fuel oil) are used, peak load, daily energy distribution and annual volumetric thermal requirement, as indicated by local energy data (Sordo and Calì [3]), and emission factors indicated in EPA database were applied; the emissions corresponding to heating were subsequently distributed on a limited number of discrete sources, whose dimensions were defined from inhabitants distribution. Afterwards it was necessary to consider the presence in Alba territory of a district heating station,

formed by four boilers and five internal combustion engines; for these apparatus the power, emission capacity, energetic production in different seasons were known. Finally, the emission of a large food production factory operating in the urban territory was considered; also in this case the emissive and operating features of the three large boilers of the plant were known. The last two emissions (district heating station and industrial plant) in the emissive scenario have been considered point sources.

On the basis of the above-mentioned considerations it was possible to define the hourly values of different nitrogen oxides emissions, and the total yearly values; in Figure 1, on the left, the percent distribution of different NOx emission sources is shown, while, on the right, as far as the traffic is concerned, the contribution of different vehicle types is reported. From these figures it is possible to verify that the traffic input, and chiefly cars, is absolutely the predominant one, as far as emitted fluxes are concerned; in the following point the effect of different sources on air quality will be discussed.

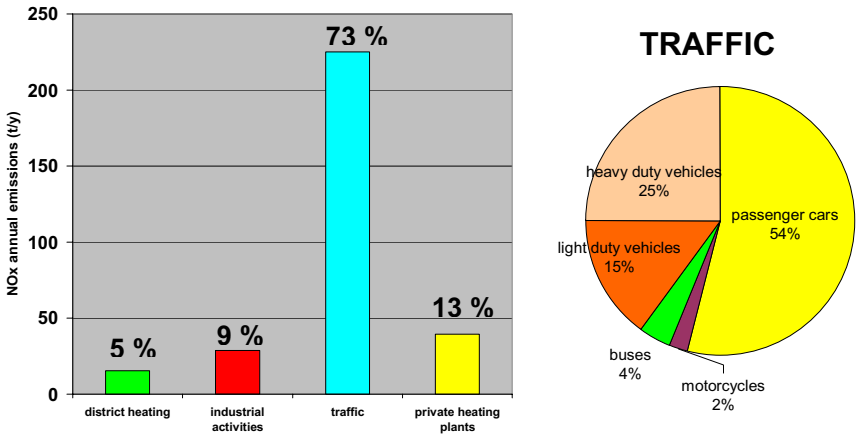

Figure 1: NOx emission sources in Alba.

3 Model calculation of environmental concentrations

In order to define environmental concentrations of NOx in different meaningful city points, it was firstly considered the possibility to use existing atmospheric dispersion models, taking into account the urban configuration where the models must be applied, and the localisation of emission points considered as sources.
As for the emissions deriving from linear traffic sources, situations where an urban canyon structure should be assumed were distinguished from more open roads conditions; in the first case the OSPM model (Berkowicz et al. [4]) has been used, as this model describes the concentration deriving from exhaust gases using a combination of a plume model for the direct contribution and a box model for the recirculating part of the pollutants in the street, because of the

vortex structure usually formed in the canyon. On the contrary for open roads the more suitable model was ISCST3 (US EPA [5]), in account of its capacity as a conventional steady-state plume Gaussian model to describe a transport and turbulent dispersion condition.

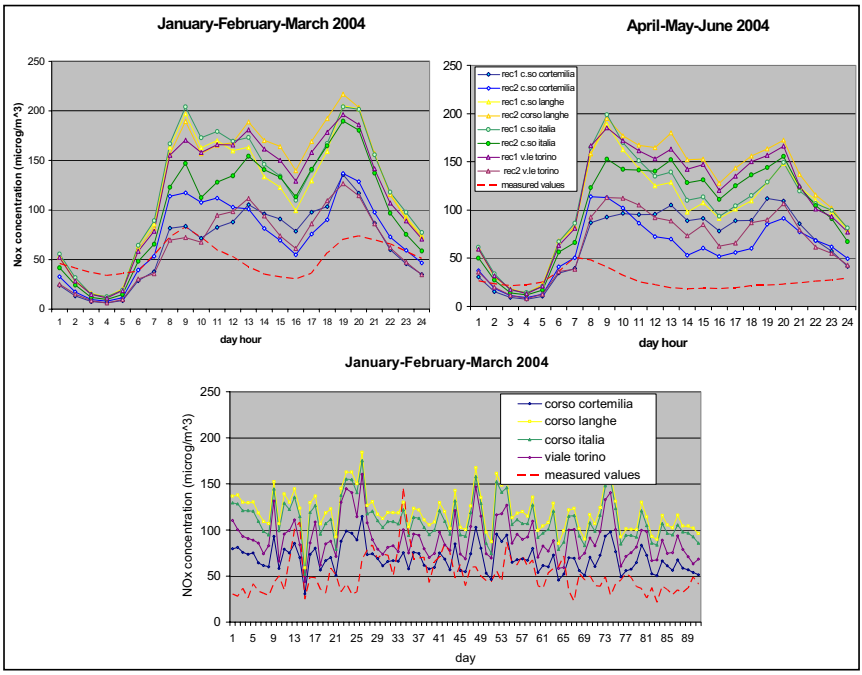

Figure 2: NOx calculated concentrations for street canyons in Alba.

In Figure 2 the results obtained by means of the OSPM model in different day hours and for different season periods are reported (for each considered street two values are reported, i.e. the leeward and the windward side of the street); in the lower part of Figure 2 the daily average concentrations are represented; in the plot the red dashed line represents the measured concentrations at the station located in a particular area of the city where the influence of local traffic is low.

As for the hourly concentration values, it is possible to establish that the calculated trends are very strictly influenced by the traffic fluxes, as maximum values are observed when the traffic peak is realized; on the contrary during the night the calculated levels are very low, when higher values could be observed for the measurements station, as a consequence of a stagnation phenomenon that cannot be represented by the steady-state type model defining the correlation between emission and concentration. The mean daily values show a similar trend, with very high differences chiefly in summer period between absolute calculated values for busy streets and measured values of the station (placed, as previously said, in a quiet zone); during the months between April and

September, the qualitative trends are similar, including relative minimum and maximum values, and so it can be confirmed the important effect of traffic contribution; during the winter, on the contrary, when the heating contribution effect cannot be disregarded, it is possible that the measured values exceed the model calculated ones.

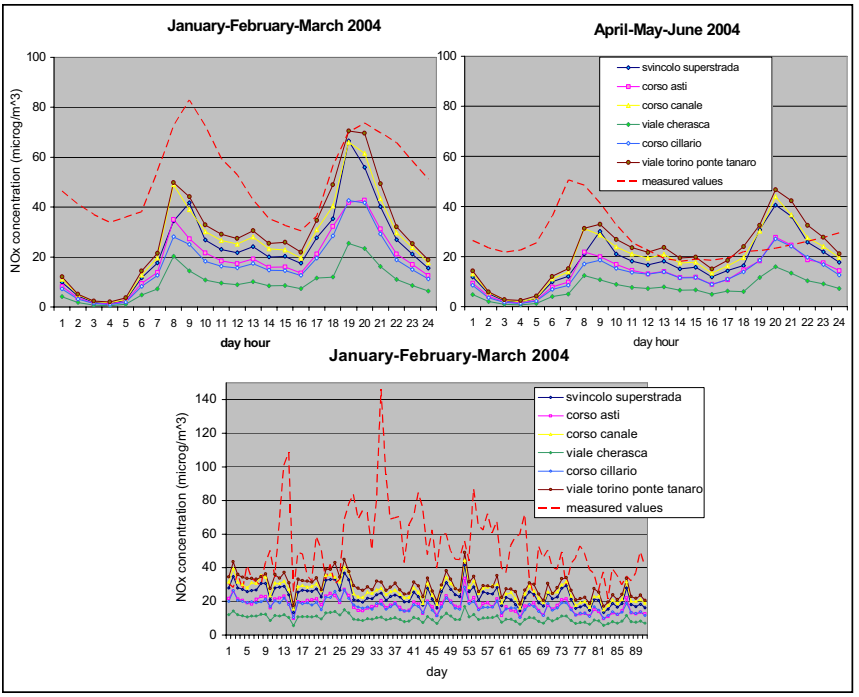

Figure 3: NOx calculated concentrations for non canyon streets in Alba.

Figure 3 reports similar results for the non canyon type, more open streets, where the ISCST3 model was used; it is possible to remark that the trend of values calculated during the day leads to lower concentrations, in account of the higher dispersion capacity of the considered zones; in the same way, as far as the daily mean values are concerned, the plots of calculated concentrations are qualitatively different from the measured ones, mainly during the winter time, and this fact is a confirmation of the different influence of source factors on the trends.

The dispersion of pollutants arising from domestic heating plants, the district heating boilers and engines and the industrial plants can be described by using ISCST3 model, taking into account the thermal plume rise effect; Figure 4 reports the seasonal mean concentrations for the domestic heating plants, whereas the concentration maps for the district heating and the industrial emissions refer to the yearly average.

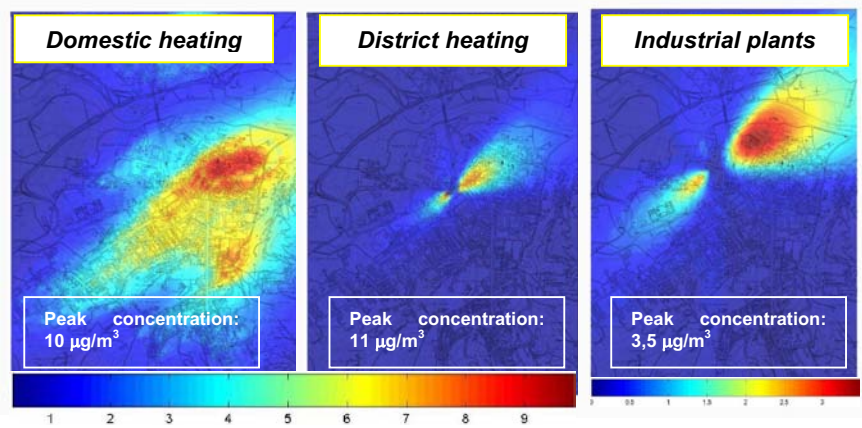

Figure 4: NOx concentration map for the other sources.

The analysis performed by using these models takes into account the effect of the actual emission on actual concentrations, but the stagnation effects are disregarded; it should be considered that the emitted substances remain for some times in the atmosphere, and they are added to the concentration that is immediately created by emitting sources. In order to individuate the background concentration, as a first approximation, we considered the concentrations measured at the station between 24 pm and 5 am, with virtually absent traffic, and the contributions from district heating system and industrial plant were subtracted. In the winter, the mean value of the difference for the 5 hours has been identified as a daily background mean value; during the summer, in order to take into account the effects of higher dispersion (larger mixing height) and photolytic transformations, it was assumed that the background contribution had a lower effect on the mean daily concentration; so the determined background concentration has been corrected by the numerical factor 5/24 during the period from May to September.

Figure 5 reports the comparison between the simulated concentrations (due to traffic, district and domestic heating, industrial sources) summed with the background concentrations calculated in the described way and the measured values for a non canyon street. As one can easily observe, in this case the results (expressed as 15 days running average) are very satisfactory; on the contrary, for a canyon street the behaviour of the calculated concentrations follows quite well the measured ones but an important shift is evident.

By taking into account the different so-defined contributions, it was possible to calculate the fraction of the total concentration due to each of them. These estimations are reported in Figure 6, in the left side for a typical canyon street, and in the right side for an open street; it is possible to observe that the traffic contribution to the determined concentration has an influence of 80% in the first configuration, and of 50% in the second one. Anyway it is necessary to take into account that the background contribution, if it is distributed in the same way as the original sources, leads to an estimation of a very low effect of the substances

deriving from fixed sources on the air quality in the examined case, and this effect is also lower if compared with their contribution in emissive terms.

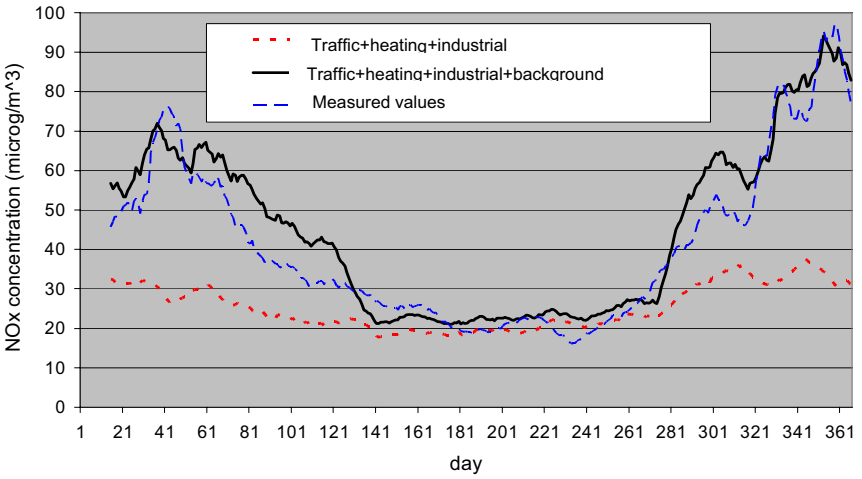

Figure 5: Comparison between calculated and measured concentrations in a non canyon street.

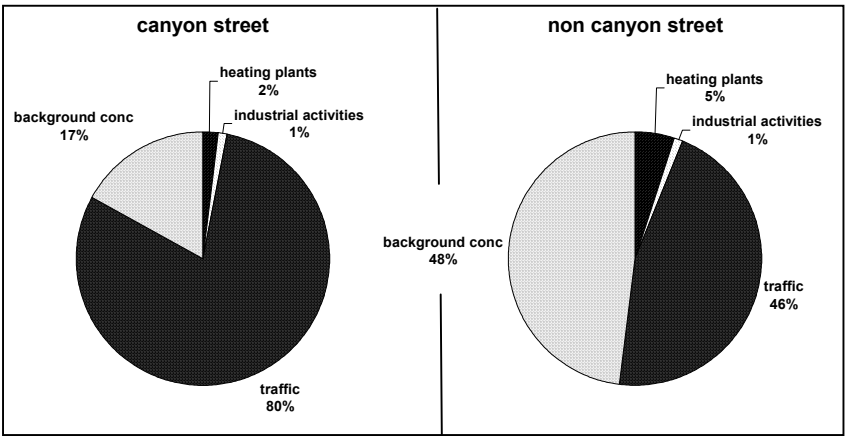

Figure 6: Contributions of different sources to the calculated concentrations.

4 Strategies for pollution reduction

The described model approach has been then used in order to put into evidence the effects of traffic limitation policies (that is the most important pollution

factor) on the air quality levels. In particular we considered the possibility, with these limitation interventions, of reducing the concentration levels below the allowed air quality limits. In order to correctly evaluate this consideration, it is in any case important to underline that the comparison can represent only a suggestion, and not a final statement, as the emission and dispersion model considers only the formed NOx, essentially in NO form, while for the air quality standards the considered parameter is NO_2; in order to obtain a more realistic comparison, we should introduce a photochemical transformation parameter, and validate this parameter on the local scale, and this aspect is not usually at disposal today; in any case it is possible to present the comparison at least as an indication and as a method illustration.

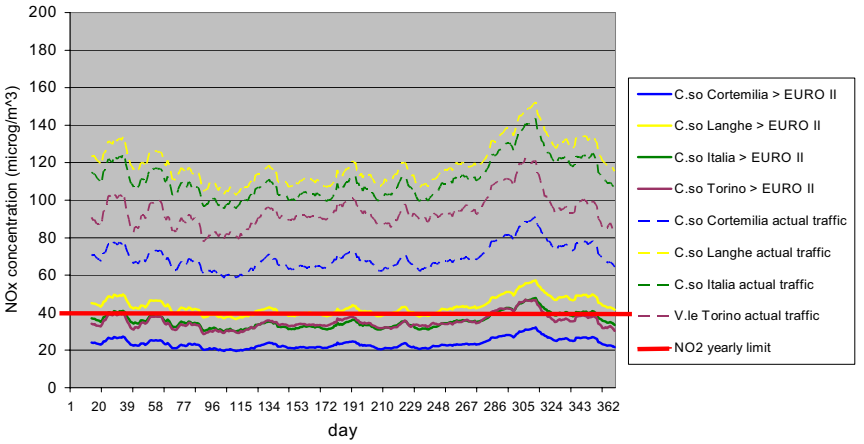

Figure 7: Effects of a traffic limitation policy on the air quality.

Figure 7 shows the results of a particular simulation, the phasing-out of the vehicles belonging to a class before EURO II; in the plot, the dashed lines report the value corresponding to unmodified car park; as it can be observed, the simulated reduction strategy allows to obtain mean year values lower than the regulation limits (40 $\mu g/m^3$), with some very limited exceptions for a particular high traffic road.

The described use of dispersion models, with the possibility of modifying the pressure factors, represents an important tool for the prediction of the effects of scenario modifications on air quality; a similar application, that cannot be reported here for space reasons, was also obtained by studying the expansion of district heating and the realisation of further cogeneration systems, located within the industrial production plant present in the town; also in this case it was interesting and meaningful to predict, on the basis of some modifications of emissive scenarios, the variation of calculated ambient concentrations, and chiefly the effects on determined maximum values.

5 Conclusions

The results of this study were able to very clearly demonstrate the critical aspects for the area taken into account, but at the same time they can be considered a methodological approach in order to evaluate pressure factors, their transfer effect, the possibilities of intervention on the origins. The strength of the traffic effect can be considered the most meaningful obtained information, and it is an important confirmation of the authorities intervention directives; it is in particular useful to extract a reasoned decision support from the results.

Within a more general point of view, as an indication of the methodologies to be used, some points requiring a deeper definition have been identified.

The emission inventory. While some parameters and some technological sources require only a careful and detailed data collection effort, for other parameters (as for example fine dusts or volatile organic substances), both the diffuse emission, (due to technological but also natural origins), and the formation mechanisms need further investigation, also by introducing experimental determinations;

Atmospheric modelling of an urban area. This aspect is very complicated in account of complex fluid dynamic regime and the particular geometry of the physical system; in account of these aspects specific studies supported by experimental validation are required in order to consolidate the knowledge of spatial and time correlation between emission scenario and concentration fields. Moreover for some not conservative parameters (the photochemical smog phenomena are an example of this aspect) the physical dispersion and convection model by itself doesn't seem enough to evaluate the pertinent phenomena.

On the basis of the above-indicated conclusions it is very important to continue the outlined studies, as they seem to be the unique valid instrument for a correct definition of intervention strategies for urban pollution problems.

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Computing mobile emissions for the Montreal area

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Abstract

A computational procedure, that takes into account climatic data and produces hourly mobile emissions of pollutants on a fine grid for the Montréal Metropolitan area has been developed for the use of Environment Canada. The procedure computes HC, CO, NO_x, CO_2, SO_2 and NH_3 mobile emissions, as well as 2.5- and 10-μm particles. The mobile emissions are calculated on the highways and main arteries of the Montreal road network. The emissions from parked vehicles are computed as well. A user friendly interface, called GRILLE, has been developed for entering parameters and launching the calculations. GRILLE calls up command files for the MOBILE 6.2C software and EMME/2 macros, which include the calculation procedure. This procedure has two parts. The first, obtains emission rates, and the second part, obtains the vehicle flows on the network and estimates the pollution on a fine grid. Results could be retrieved as simple text format or as graphic output. The emission computations can be done for any day and any hour of the year. Use of the model by Environment Canada is described as well.
Keywords: mobile emissions, emission rates, network vehicle flows, fine grid.

1 Introduction

This paper reports the results of a project entitled, "Calculation of Mobile Emissions on a Fine Grid – Pilot Project in the Montréal Area," that was carried out jointly by the Ministère des Transports du Québec (MTQ), Environment Canada and the Centre de Recherche sur les Transports (CRT) of the Université de Montréal. The aim was to compute, on a very fine scale, the atmospheric

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emissions generated by road transportation in the Montreal area. This project would serve as a pilot for applications to other major urban centres in Canada.

Specifically, the objective of the project was to develop a procedure that would take data entered in meteorological fields on an hourly basis, on which mobile emissions are based, and to provide emissions of the main atmospheric pollutants on a regular grid covering the greater Montréal area, with a resolution of 1 km.

The MTQ maintains the Montreal Area Transportation Model (MOTREM), a transportation planning model, by using the EMME/2 software. The procedure had to calculate emissions using the MOBILE6.2C software (the Canadian version of MOBILE6.2) and the vehicle flows computed by EMME/2.

The model developed meets these expectations and does so efficiently.

2 The proposed model

This section provides a summary of the various elements of the model. For a complete description of the model see CRT [1].

2.1 Basic characteristics

The pollutants and emissions to be evaluated are listed in Table 1.

Emissions are calculated on an hourly basis for the 28 types of vehicles in MOBILE6.2C (for more details on MOBILE6.2 see USEPA [4]), with evaluations for one or 14 speeds on freeways and main arteries, as specified in the same table.

The model calculate HC, CO, NO_x, CO_2, SO_2 and NH_3 pollutant emissions, as well as 2.5 and 10 μm Particulate Matters : SO_4, Organic Carbon of Diesel (OCARBON), Elemental Carbon of Diesel (ECARBON), Total Carbon of Gasoline (GASPM), BRAKEWEAR, TIREWEAR and TOTAL.

Except for BRAKEWEAR and TIREWEAR, these are exhaust emissions. For HC, CO and NO_x, exhaust emissions on start up are also calculated. The model also determines HC evaporative emissions: Hotsoak, Diurnal, Resting, Running Loss and Crankcase. Some of these emissions are produced when vehicles are parked.

Emission rates by MOBILE6.2C vehicle types are aggregated into the four types of MOTREM vehicles considered: Autos, Regular Trucks, Heavy Trucks and Buses. The eight MOTREM road types are classified on freeways and arterial roads.

Emission rate/speed functions generated from evaluations for 14 speeds by MOBILE6.2C are used to determine by interpolation emissions for all the speeds that are computed by the transportation model on the road network.

2.2 Benefits

The developed procedures have the following benefits.

Table 1: Emissions estimated using MOBILE6.2C.

POLLUTANT	EMISSION		VEHICLE	ROAD	SPEEDS
HC (VOC)	RUNNING		ALL VEHICLES	FREEWAY and ARTERIAL [1]	14
	START		LD + MC	ALL ROAD [2]	1 *
	HOTSOAK		G + MC	ALL ROAD	1
	DIURNAL		G + MC	ALL ROAD	1
	RESTING		G + MC	ALL ROAD	1
	RUNLOSS		G - MC	FREEWAY and ARTERIAL	14
	CRANKCASE		G + MC	ALL ROAD	1
CO	RUNNING		ALL VEHICLES	FREEWAY and ARTERIAL	14
	START		LD + MC	ALL ROAD	1
NO_X	RUNNING		ALL VEHICLES	FREEWAY and ARTERIAL	14
	START		LD + MC	ALL ROAD	1
CO_2	RUNNING		ALL VEHICLES	FREEWAY or ARTERIAL [3]	1
SO_2	RUNNING		ALL VEHICLES	FREEWAY or ARTERIAL	14
NH_3	RUNNING		ALL VEHICLES	FREEWAY or ARTERIAL	1
		PM			
SO_4	RUNNING	2.5 10	ALL VEHICLES	FREEWAY or ARTERIAL	14
OCARBON	RUNNING	2.5 10	ALL VEHICLES	FREEWAY or ARTERIAL	1
ECARBON	RUNNING	2.5 10	ALL VEHICLES	FREEWAY or ARTERIAL	1
GASPM	RUNNING	2.5 10	ALL VEHICLES	FREEWAY or ARTERIAL	1
LEAD	RUNNING	2.5 10	ALL VEHICLES	FREEWAY or ARTERIAL	1
BRAKE WEAR	BRAKE WEAR	2.5 10	1 VEHICLE	ALL ROAD	1
TIRE WEAR	TIRE WEAR	2.5 10	ALL VEHICLES	ALL ROAD	1

1 FREEWAY and ARTERIAL. The rates are different.

2 ALLROAD. MOBILE62 uses a single rate.

3 FREEWAY or ARTERIAL. The rates are the same.

* 1 speed. The rate does not depend on speed. LD = Light Duty; G = Gasoline; MC = Motorcycle

2.2.1 User-friendly data-entry interface

The model uses a user-friendly interface called GRILLE for the entry of input parameters and to launch executions. It was developed in Java in a Windows environment. Input parameters in GRILLE are organized into five groups: date and time of the evaluation, external conditions, fuel characteristics, advanced options and cells on the grid. Figure 1 shows GRILLE's main window.

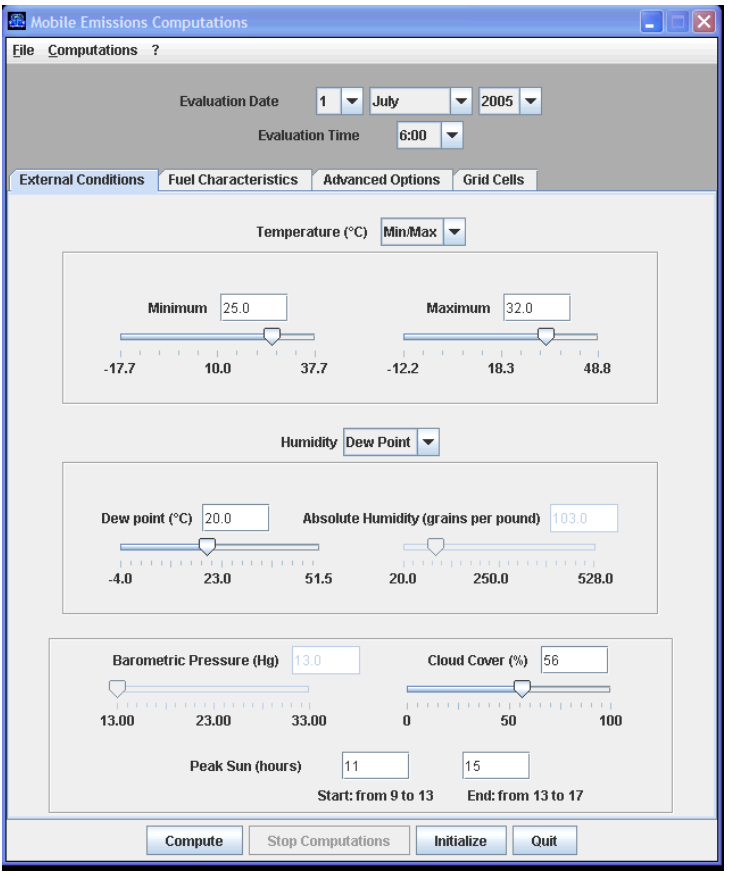

Figure 1: GRILLE's window.

The date and time of the evaluation are crucial parameters. They allow identifying other input parameters in the model in a manner that is transparent for the user.

External conditions include the meteorological data needed for MOBILE6.2C to estimate emissions. These conditions are temperature, humidity, barometric pressure, cloud cover, peak sun and sunrise/sunset hours. These are the data that the user is most interested in manipulating to determine the pollution emitted under various weather conditions.

Fuel characteristics refer to the level of sulfur in the fuel and the Reid Vapour Pressure (RVP) factor. The default values allowed by Environment Canada are saved in a file and accessed directly by GRILLE.

The advanced options allow two elements, which are not integrated in the computations to be evaluated: government programs and oxygenated fuel.

Finally, the cells of the grid can be defined by the user in terms of size (width and height) and location (horizontal and vertical offsets).

2.2.2 Efficiency in the use of related software

MOBILE6.2C can be used to generate emission estimates separately by average speed, roadway type and vehicle class. These disaggregated values can be post-processed for various aggregations of the emissions estimates that are required.

The model uses the ability of MOBILE6.2C to calculate, in a single step, all types of emissions for all pollutants and all types of vehicles, for one type of road and one size of particulate, for one speed (the particulate estimation is independent of the estimation of other pollutants). The number of executions in MOBILE6.2C in an hourly evaluation is reduced to two cases: Freeway with 10 μm Particulates and Arterial with 2.5 μm Particulates. Two evaluations are also required for months other than January or July (the only choices of MOBILE6.2C).

2.2.3 Possibility of estimating pollution for any time of day, week, Saturday or Sunday, and any month of the year

The travel information provided by MTQ corresponds to the five MOTREM periods of the day (am peak, mid-day off-peak, pm peak, evening off-peak and night) for a typical fall week. The scope of this project is to estimate road traffic on an hourly basis for weekdays and weekends and for all months of the year.

An analysis of the road counts (obtained from the MTQ's CIR-6002 system database) provides the information needed to determine travel distribution patterns throughout the year, the week and the day.

Given that travel patterns are different for each type of vehicle, the analysis deals only with data disaggregated by type of vehicle.

Vehicle by period flows for a typical fall day are adjusted by these distributions patterns in order to reflect hourly traffic conditions on a weekday, Saturday or Sunday and for any month of the year.

2.3 Limitations

The inputs for MOBILE6.2C lack of information developed specifically for the Montréal area. We must repeatedly use default U. S. values.

Other MOBILE6.2C limitations, such as the admissible range of temperatures (from -17.7 to 48.8^{o} Celsius) do not allow the model to be fully adapted to the conditions of the Montréal area. The lowest temperatures in the Montreal area are of the order of -30^{o} Celsius.

When aggregating emissions from various types of vehicles into a single vehicle, due to a lack of data, we must suppose that all vehicles travel the same number of kilometres per year.

The results obtained for emissions calculated at centroids for Saturdays and Sundays should be used with care because they are obtained using traffic distribution factors and not with information regarding personal travel. The same reservation applies to holiday periods.

3 General computation procedure

The general computation procedure consists of two main parts, "Obtaining emission rates" and "Obtaining network flows and estimating pollution on a fine

grid." Figures 2 and 3 show the steps taken in the calculation procedure, including input and output elements.

3.1 Obtaining emission rates

The purpose of this part is to create input files for the MOBILE6.2C software, extract emission rates from the same software's output files and incorporate the rates into the functions to be used by EMME/2 in the second part of the procedure (for details on EMME/2 see INRO [3]).

"Obtaining the emissions rates" begins when the user requests an execution in the GRILLE interface. First, the data the user provides to GRILLE is saved to a file and then integrated into the MOBILE6.2C input files. Several input files are created in this way due to the range of emissions to be calculated. MOBILE6.2C is launched.

The MOBILE6.2C output file containing the desired results depends on the emission to be retrieved. Running, Running loss, Crankcase and Particulate Matters emissions rates (required in grams/km) are obtained directly from the descriptive output files, while Start and Hot soak, Resting and Diurnal emissions rates (required in grams/vehicle or grams/hour) are obtained in a disaggregated manner and must be calculated in a data processing environment.

Once the emission rates are retrieved for each of the 28 types of vehicles, they are aggregated by the four MOTREM types. In the event that two evaluations are required (when the evaluation month is different of January and July), the results for the two months are combined in order to obtain emission rates for the desired month.

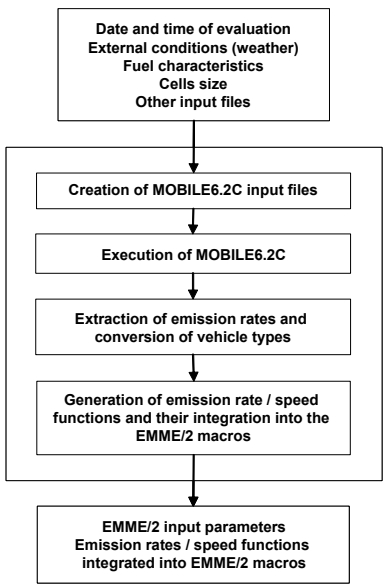

Figure 2: Obtaining emission rates, flow diagram.

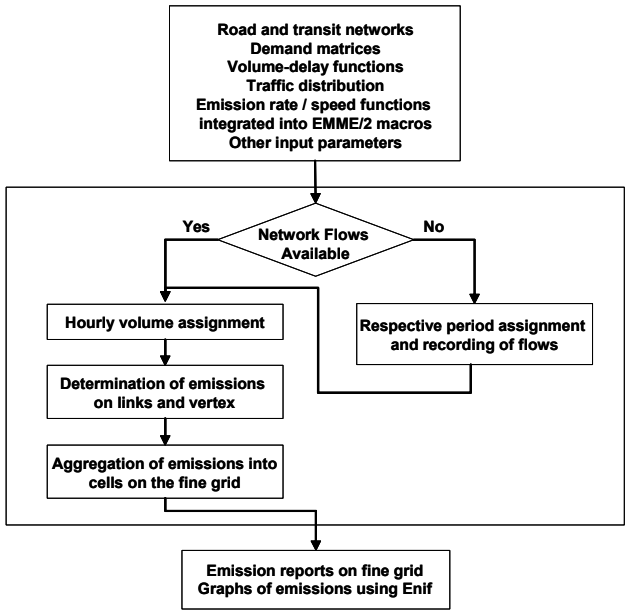

Figure 3: Obtaining network flows and estimating pollution on a fine grid, flow diagram.

Depending on the type of emission, the rate may be a constant or based on speed. In both cases, the rates are converted to mathematical expressions in an EMME/2 macro procedure for later use. For emissions for which rates vary by the type of road, two functions are generated.

3.2 Obtaining network flows and estimating pollution on a fine grid

The purpose of this part is to determine the flow of vehicles on the road network, associate previously calculated emissions rates with that flow and quantify existing pollution in the cells of a fine grid. This part is performed by using the EMME/2 software and the MOTREM data bank.

In "Obtain network flows and estimating pollution on a fine grid" one of two routines will be launched.

3.2.1 Flows not available

If vehicle flows are not available for the year, season (summer or other), day (weekday, Saturday or Sunday) and desired MOTREM period (period associated with the evaluation hour), vehicles are assigned by period. The year, season, day and period of the day are needed to choose the demand, auto network and transit network to be used in the assignment.

The period assignment process, as set forth below, is based on the one used by the MTQ.

1. Initialization, Buses as fixed volume on links
2. Auto assignment in a single class
3. Heavy Truck assignment with generalised costs. Travel time is the average of the all-or-nothing time and the Auto travel time.
4. Update of fixed volumes to include Heavy Truck volumes
5. Multi-class Auto - Regular Truck assignment

Vehicle flows and aggregated demand at origins and destinations are stored for later use.

3.2.2 Flows available

If the flows are already available, period to hour factors are applied to them and to the demand. Flows for all types of vehicles are merged as a fixed flow on links. Then a no demand, all-or-nothing hourly assignment is performed.

The speed of vehicles is calculated on links. Then emissions rates are associated with vehicles moving at different speeds, and pollution is determined at links and centroids.

Finally, the GRTOOL program is launched. For each link (and centroid) pollutant it splits the pollution according to the overlap with different grid cells. Then GRTOOL accumulates the pollution for each cell on the grid. These results are saved in the final results files.

4 Preliminary results

Figures 4 and 5, obtained using the graphical interface Enif, show the emissions of HC (VOC) on a fine grid for the Montréal area.

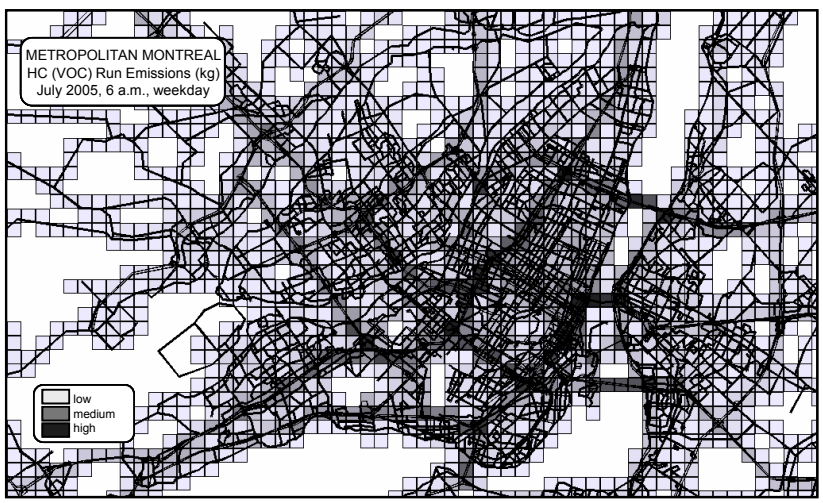

Figure 4: HC (VOC) run emissions (kg).

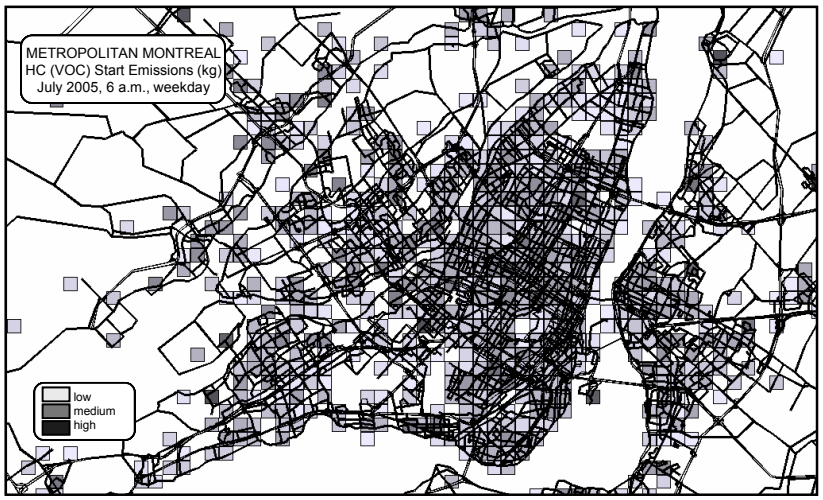

Figure 5: HC (VOC) start emissions (kg).

5 Simulation of a smog episode with GRILLE

The Meteorological Service of Canada evaluated GRILLE during a regional smog episode of 2001 in the Montreal area. The simulated episode started on 30 July and ended on 5th August 2001, with 2nd August being a day where southern Quebec experienced a regional smog episode, the 8-hour running average of ozone concentrations exceeding the 65 ppb threshold of the Canada-wide Standard at several monitoring locations.

Quebec experienced a regional smog episode, the 8-hour running average of ozone concentrations exceeding the 65 ppb threshold of the Canada-wide Standard at several monitoring locations.

The air quality model used in this study was the Canadian AURAMS model, Gong et al [2]. AURAMS is mainly used to simulate smog (ozone and $PM_{2.5}$) and dry and wet deposition (acid rain). The AURAMS air quality model is integrated twice on a domain covering North-eastern North America. The first run uses the regular SMOKE (Sparse Matrix Operator Kernel Emissions; available from the US EPA) on-road vehicle emissions based on the 2000 Canadian inventory. This input file was then modified for the second run; the emissions generated by GRILLE were aggregated on the 21-km model grid and replaced the SMOKE-generated data over the Greater Montreal region.

The daily maximum ozone concentrations predicted by the AURAMS model on 2nd August 2001 from the two scenarios differs as would be expected. The ozone concentrations increase from 3 to 5 ppb downwind of Montreal in a narrow plume. This is due to the fact that the GRILLE emissions are better distributed spatially with a more pronounced and sharper peak over Montreal itself and reduced emissions in the suburbs. These reduced emissions in the periphery lead to a decrease in ozone on each side of the central plume. A second

factor responsible for the difference is the change in the emission rates, the decrease in NOx emissions expected to lead to an overall reduction in ozone concentrations.

The reported daily maximum ozone concentrations from 11 monitors in Southern Quebec were compared to the AURAMS values for the two emission scenarios. Common statistics between the model and observations are shown on table 2. It shows that the use of GRILLE to compute the on-road vehicle emissions has significant benefits for ozone prediction near Montreal and downwind. It reduces the bias and gives better correlation, the root mean square error is reduced and the variability of the model is closer to the observations.

Table 2: Model statistics for the prediction of the daily maximum ozone concentration (66 model-observation pairs).

	GRILLE	SMOKE
Bias (ppb)	-1.68	-3.09
Correlation coefficient	0.36	0.24
Normalized standard deviation	0.66	0.58
Centered root mean square error (ppb)	18.9	19.8

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Renewable energy impact in reducing greenhouse gas emissions at local scale: the case study of South Tuscany geothermal fields

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Abstract

The energy sector is responsible for the majority of greenhouse gas emissions that cause global warming. The development of renewable energy is a central aim of the European Commission's energy policy. Italy has the principal high temperature geothermal deposits in the EU and alone represents 97.9% of the total European capacity in 2004. Tuscany has already reached the European goal of 25% of RES (Renewable Energy Source) established for 2010, thanks to the geothermal energy presence in its territory. Geothermal energy production in the South Tuscany area, which falls into the Siena and Grosseto Provinces, has been developed since 1969 and in 2004 had 2,360 GWh of net energy production. The aim of this paper is to point out the importance of geothermal energy in reducing greenhouse gases emissions at a local scale, carrying out emissions inventories of the concerned Provinces with the IPCC methodology. The electrical energy production in 2000 was enough to cover all the electrical energy consumptions in both Provinces. Applying a strictly geographical approach to the electrical energy consumption, the greenhouse gas net balances for both the Provinces decrease more than 50% that if we use a responsibility one.
Keywords: greenhouse gas emissions inventory, local scale, renewable energy, geothermal energy, IPCC methodology.

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1 Introduction

The coming into force of the Kyoto Protocol in 2005 imposes to the signatory Nations to activate all the measures needed for the control and the reduction of greenhouse gas emissions, till a global average cut of 5.2% of 1990 emissions in the period 2008-2012. Renewable Energy Sources (RES) will play in next years a focal rule in reducing the greenhouse gas emissions [1]. RES can help in slowing down the emissions rate from energy sector, the main source of CO_2 emissions, due principally to fuels combustion, both for direct use, for transport, residential and industrial use and for electrical energy production in thermoelectric power stations.

European Union put in the strategy for the emissions reduction the substitution of fossil fuels with renewable energies. The aim of the White Paper in 1997 was to attain, by 2010, a minimum penetration of 12% of renewable energy sources in the European Union. Then the European Parliament and the Council issued the directive 2001/77/EC to facilitate a significant increase in the medium term in renewable generated electricity (RES-E).

Few European Countries have the natural resources necessary for electrical valorization of geothermal energy. Total geothermal gross generation in Europe in 2004 amounts to 5,545 GWh. Italy has the principal high temperature geothermal deposits in the EU, 5,430 GWh gross production, and alone represented 97.9% of total European capacity in the same year [2]. Geothermal energy production in Italy in 2004 is 5,127 GWh of net production and constitutes the 1.8% of the national net production for that year.

Geothermal energy production is totally located in Tuscany, in two areas, the first is Larderello zone, where geothermal potentiality as electrical energy source was discovered in 1904, and the second in the South, near Mt. Amiata. This area and Travale-Radicondoli fields are included administratively in two Provinces, Siena and Grosseto.

1.1 Geothermal energy in Siena and Grosseto Provinces

Siena and Grosseto Provinces are located in the part of Tuscany with the lower inhabitant's density, respectively 66 and 47 inhab/km^2, and their economy based on tertiary and tourism, with an important rule also for agriculture, especially for Grosseto. In the core of this area there are the geothermal fields at foots of Amiata Mountain and in the north of Siena Province the Travale Radicondoli fields.

In South Tuscany geothermal fields have been exploited since the beginning of 20th century and in 2004 five geothermal power plants were in operation, with total net production of 2,360 GWh [3]. These are the only power plants in the two Provinces and all the electricity produced is put in the national distribution network. Direct use of geothermal energy as heat pump systems is not very developed at the moment, the main use is for a greenhouse farm, so this use will not be included in this study, focussing the attention on electrical use only.

Geothermal energy has in this zone a slow but constant development, and how we can see in Figure 1, Grosseto Province reaches the production of Siena, being over the electrical energy consumption in the last years. Only for 2000 the only geothermal generation is adequate to sustain all the provincial consumption (industrial, residential tertiary and agriculture use) for both the areas. This energy production becomes important at regional scale, where RES are already the 27% of total energy production.

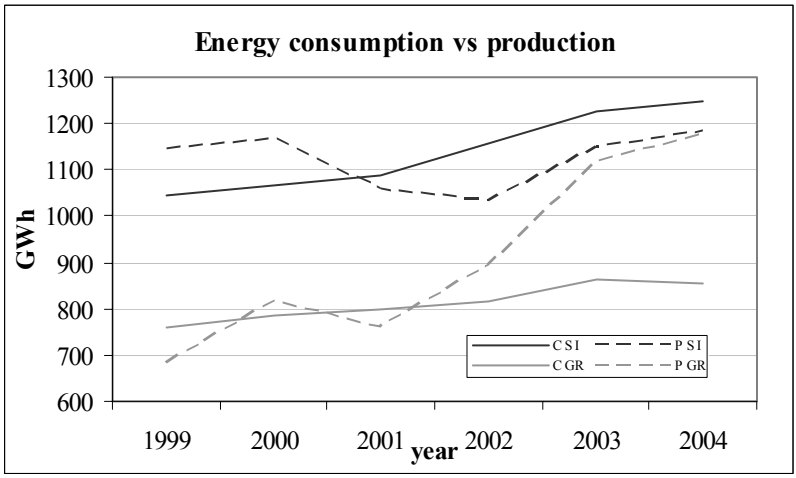

Figure 1: Electrical consumption (C) and geothermal energy production (P) in 2000 for Siena (SI) and Grosseto (GR) Provinces (GWh) [3].

This renewable energy generation can be evaluated in term of emissions saving utilizing IPCC methodology for an emissions inventory at local scale [4].

The greenhouse gas inventories of Siena and Grosseto Provinces have been developed for year 2000, the year in which the geothermal generation can cover all the electrical consumption in the two Provinces at the same time and the emission saving is the maximum possible in the whole area.

The IPCC methodology, based on a geographical approach, has been used for the five sectors of emissions sources (Energy, Industry, Agriculture, Waste and Forestry). This approach has been important most of all in energy sector, to evaluate the emissions of electrical energy generation. Indeed, for a local inventory is possible to recorder the electrical energy consumption on the base of local energy production or considering all the electrical energy utilized from the mix in national network. The strictly geographical approach has made possible to attribute geothermal energy production to the correspondent Provinces, whereas this energy is put in the national electrical network and is not really used in loco.

The problem concerns the adoption of a territorial or responsibility approach in the allocation of the emissions [5] and this choice may become important especially at small scale, where the exchanges with the outside become bigger than the internal ones.

The aim of this paper is to evaluate the importance of this emission saving, comparing to the other emission sources, considering both the approaches, the territorial and the responsibility one.

2 Methods

The IPCC methodology have been used to point out greenhouse gases emissions inventories, on the base of Revised Guideline 1996 [6] with the update "Good Practice Guidance and Uncertainty Management" [7] and the "Good Practice Guidance for Land Use, Land-Use Change and Forestry" [8].

The GWP value in CO_2eq for CH_4 and N_2O used is the established ones in the Third Assessment Report (TAR) of 2001, respectively 23 for CH_4 and 296 for N_2O.

As a first result we show emission inventories developed considering the electrical consumption from national mix. In a second balance, geothermal energy production has been considered used in the two Provinces in accordance with a strictly geographical approach.

2.1 Input data

It has been possible to use, for the majority of the emissions sources, data at local scale, from the national data base and reports for year 2000.

In the energy sector we consider the emissions produced by direct combustion of fuels and electrical energy consumption. This is not a double counting case because in the two Provinces there are no power plants except for the geothermal ones. An average value of greenhouse gas production in kg CO_2eq/kWh has been estimated starting from the national amount of fuels consumed for power production [9]. Data on fuels and energy consumption are on provincial scale [10]. Only for Siena Province, is considered in energy sector the combustion emissions from an incinerator plant with energy saving [11].

Siena and Grosseto Provinces have a prosperous agricultural activity, so this is an important sector. Data both for animal breeding and management as well as from fertilizers and manure use are from Agriculture Census 2000 [12] at provincial scale.

Waste and wastewater production and management data have been found in nation reports [11] with data at provincial scale for solid waste disposals, wastewater purification treatments. Up to now Grosseto has an incinerator plant without energy saving.

The industrial sector is not relevant for Grosseto Province greenhouse emissions and for Siena the only industry considered is the crystal production in Colle Val d'Elsa [13] that cover by itself the 15% the worldwide production and the 95% of the Italian.

For the CO_2 absorption by forest annual growth Regional Forest Inventory 1998 [14] has been used for woodland in ha and we used also a local measured value for the woods growth rate (Table 1).

South Tuscany forests are typically constituted by oak woods and Mediterranean shrublands. Provincial Section of State Forestry Department data have been used for forest exploitation in 2000 in t 10^3 for wood type.

In the first balance we used the IPCC procedure and we obtained the net emissions subtracting forest absorption from total emissions and using the national emission for GWh for electrical energy consumption. In the second balance we adopt a strictly geographical approach for electrical energy consumption. We have considered electrical production from geothermal used in loco, so the electrical consumption of the Provinces covered from geothermal production is not considered in the inventory.

Table 1: Wood type and annual rate growth m^3 dm/year [14].

	Forest surface %		
Wood type	**SI**	**GR**	**Rate growth m^3 dm/year**
Turkey oak	36.32	30.03	6.4
Holm-oak	12.18	8.07	5.8
Pubescent Oak	19.07	7.57	4.7
Chestnut	5.10	4.55	9.1
Beech	0.65	1.17	9.9
Hornbeam	0.73	1.72	5.6
Other woods	8.56	8.26	4.6
Mediterranean scrubland	17.39	38.63	2.6

3 Results and discussion

The greenhouse gas emissions have been estimated on the base of IPCC methodology for the five sectors for year 2000. The first balance, with electrical energy emissions included, is presented in Tables 2; the indirect greenhouse gases are reported out of the balance calculation.

As it is shown in the tables, energy sector is largely the most important source of emissions in both Provinces, due also to the very low industries presence. We discuss energy sector in detail in the next section.

The second sector for importance is waste sector for CH_4 emissions from solid waste disposal sites and wastewater treatments. Siena has a lower CH_4 production despite the higher population due to a lower waste production and a higher urban waste differentiated collection.

Then in the agricultural sector both N_2O emissions from fertilizers use and CH_4 from breeding enteric fermentation are significant. In this case the higher emissions in Grosseto Province depend on the main weight of agriculture in the economy of this area.

The industry sector is not significant in both the Province, based principally on tertiary sector, tourism and in second play on agriculture. Only in Siena Province is relevant crystal production that has as process emissions NMVOC.

The role of CO_2 adsorption by forests is very important in the two Provinces, since both have 41% of the territory covered by forest lands, and this CO_2 abatement arises to cover almost all the CO_2 emissions from energy sector.

The index t CO_2eq/inab resumes all this emissions in base to the Province population, and Grosseto has a lower index value, due mainly to minor energy consumption. The ratio between MWh of electrical energy consumption and population is 4.2 for Siena and 3.7 for Grosseto.

Table 2: Siena and Grosseto emission balances in 2000 (Gg CO_2 eq).

Siena	CO_2	CH_4	N_2O	NO_2	NO_x	CO	NMVOC	Total
	Gg	Gg CO_2 eq	Gg CO_2 eq	Gg	Gg	Gg	Gg	Gg CO_2 eq.
Energy	1,574.7	3.7	2.9	*0.010*	*6.930*	*39.562*	*7.495*	1,581.3
Agriculture	0.0	60.3	188.1	*0.635*	*0.035*	*0.931*		248.4
Waste	0.0	347.6	2.3	*0.008*				349.9
Forest	-1,135.4							
Industry	0.0	0.0	0.0				*0.077*	
Total emissions Gg CO_2 eq								2,179.5
Total net emissions Gg CO_2 eq								1,044.3
t CO_2 eq. /inhab.								4.11

Grosseto	CO_2	CH_4	N_2O	NO_2	NO_x	CO	NMVOC	Total
	Gg	Gg CO_2eq.	Gg CO_2 eq.	Gg	Gg	Gg	Gg	Gg CO_2 eq.
Energy	1,130.8	2.8	2.2	*0.007*	*5.148*	*32.280*	*6.095*	1135.7
Agriculture	0.0	124.7	195.9	*0.662*	*0.034*	*0.922*		320.6
Waste	2.5	378.6	2.0	*0.007*				383.2
Forest	-1,079.7							
Industry	0.0	0.0	0.0					
Total emissions Gg CO_2 eq								1839.5
Total net emissions Gg CO_2 eq								759.8
t CO_2 eq. /inhab								3.5

3.1 Energy sector

The energy sector emissions are constituted by fuel combustion and electrical energy consumption, plus incinerator emissions for Siena Province. The majority of all the emissions are from fuels combustion, with 63.8% for Siena and 63% for Grosseto of all the energy emissions. The fuel direct combustion includes commercial, industrial, domestic, agricultural and transport that is the main use, as we see for Siena in Figure 2.

The lasting energy emissions (36% and 37%) are emitted by electrical production of energy consumed by the Provinces, calculated from average national emissions in Gg CO_2eq for GWh. In 2000 the national electrical production has been obtained 79.7% thermoelectrically, 18.8% hydroelectrically, 1.7% by geothermal energy and 0.2% by wind ad solar. The emission factor for electrical energy in 2000 is 0.528 Gg/GWh CO_2eq, and it has then been multiplied for provincial electrical consumption. In Figure 3 Gg CO_2eq emissions from electrical energy consumption by sector for Siena Province are shown.

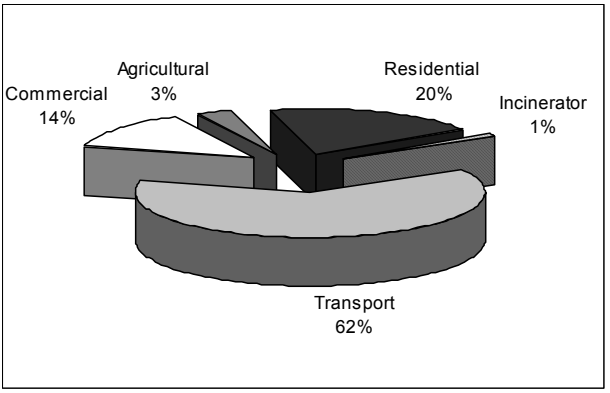

Figure 2: Total fuels emissions in Siena Province in 2000 by sector.

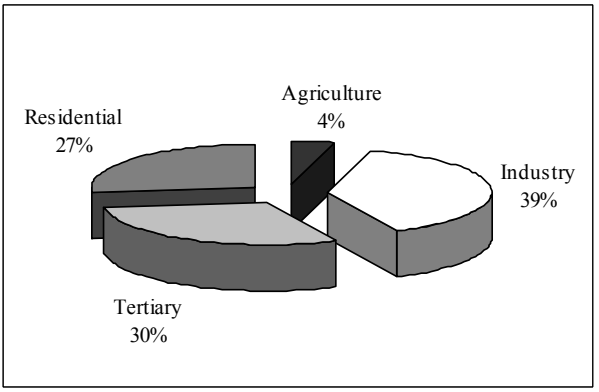

Figure 3: Gg CO_2eq emissions from electrical energy consumption by sector for Siena Province in 2000.

The total energy sector emissions are 73% for Siena and 62% for Grosseto on total emissions inventoried. The only electricity consumption emissions are equal respectively to 26% (SI) and 23% (GR) on the total emissions value (Table 3).

If now a strictly geographical approach is used for electrical consumption in both Provinces and all the geothermal production is attributed to the area where the power plants are collocated, we can outline a new emissions balance.

Taking into consideration the geothermal power plants production and the electrical consumption trend from 1999 to 2004, shown in Figure 1, we see a complete coverage for provincial electricity consumption for year 2000.

Table 3: Energy sector detail for Siena and Grosseto Provinces.

Energy sector emissions (Gg CO_2eq)	SI	GR
Fuel combustion	1016.4	719.5
Electricity	564.8	416.3
Total Energy	1581.2	1135.7
Total emissions	**2,179.5**	**1839.5**
Energy sector	73%	62%
Electrical energy consumption	26%	23%

In this way, the emissions reduction is equal to the total emissions from electricity consumption.

The new net balance becomes 479.3 Gg CO_2eq with 1.89 t CO_2eq /inhab for Siena and 343.5 Gg CO_2eq with 1.59 t CO_2eq /inhab for Grosseto (Figure 4). The reduction in the second net balance is equal to 54% in both Provinces, and the new values for t CO_2eq /inhab are very low compared to other Italian Provinces.

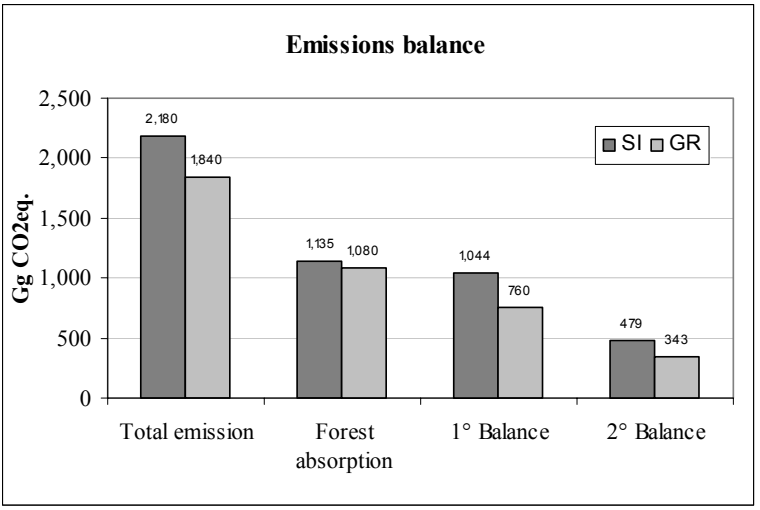

Figure 4: Greenhouse gas emissions inventories for Siena and Grosseto Provinces.

4 Conclusions

We have demonstrated how the approach chosen in draw up electrical energy consumption in a greenhouse gas emissions inventory can change to a great degree the emissions balance. In our case, applying this assumption to electrical energy consumption to a country with a renewable energy source in its territory, we can see an important difference.

The variation in result in applying a responsibility approach and then a strictly geographical approach to electrical energy consumption is over the 54% of the net balance, indeed, the two Provinces became autonomous for electrical energy for year 2000.

The comparison between the two approaches may be useful at local scale to comprise the real situation of greenhouse gas emissions. The results can help in identifying the sectors responsible of the real local emissions and consequently the sectors where further reductions are possible.

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Wood processing as a source of terpene emissions compared to natural sources

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Abstract

The aim of this paper is to analyse the importance of terpene emissions from forestry and the wood industry and relate these anthropogenic emissions to the natural terpene emissions from undisturbed forests. Biogenic volatile organic compounds are emitted naturally from trees and other plants. Boreal forests are dominated by terpene-emitting tree species. Anthropogenic terpene emissions occur due to drying, machining and tooling of wood. This is a cause of concern with regulatory authorities faced with expanding production of biofuels, e.g. wood pellets. Anthropogenic terpene emissions are of current importance as the use of biofuels has increased considerably over the recent years. The most important environmental effects of terpene emissions are due to the formation of photo-oxidants and atmospheric aerosols. Photo-oxidants cause forest and crop damage, and are harmful to humans. Carbonaceous aerosols have an impact on climate change. Furthermore, most sesquiterpenes are used in the chemical communication systems of various insects. There are also issues concerning the working environment in the wood industry. Environmental effects of terpene emissions are analysed with focus on three key aspects: the total amount of emissions, the concentration in air and the types of terpenes emitted. The reported concentrations of monoterpenes are in most cases below the occupational exposure limits, with drum barking and pellets production from non-dried sawdust close to the limit. Anthropogenically emitted terpenes have a higher proportion of sesquiterpenes than naturally emitted terpenes have, especially when the processing of wood involves elevated temperatures.
Keywords: terpenes, VOC, spruce, pine, sawmill, drying, wood, biofuel, pellets, sawdust.

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1 Introduction

There is a growing concern about terpene emissions from the wood industry. Terpene emissions contribute to several different environmental problems, and have an impact on work environment. Anthropogenic emissions are studied in order to estimate effects on local atmospheric chemistry, assess the suitability of different process procedures, and see where efforts should be focused in order to decrease emissions. They should be seen in relation to the natural emissions where environmental effects are concerned. I focus on the situation in the northern hemisphere, the European boreal region, where the main species are Scots pine, Norway spruce and Silver birch. Biofuel in this region is almost exclusively made from spruce and pine.

1.1 Terpenes

Terpenes are primarily found in resin the heartwood and sapwood of softwoods (conifers), and in the sapwood of hardwoods (deciduous trees). Terpenes are also stored in special cells in the needles of conifers and leaves of deciduous trees. In softwoods, the terpene group consists mostly of monoterpenes ($C_{10}H_{16}$), sesquiterpenes ($C_{15}H_{24}$) and diterpenes ($C_{20}H_{32}$), whereas triterpenes and sterols dominate in hardwoods. Terpenes have several protective functions in plants. They neutralize ozone that would disturb photosynthesis. They repel many insects and herbivores (terpenes attract both beetles and their predators). They also lower the viscosity of resin, making it possible for resin to flow to a damaged part of the plant. There the volatile mono- and sesquiterpenes are emitted to air and the non-volatile diterpenoic resin acids are left as a hydrophobic cover, protecting the tree from further damage.

1.2 Environmental issues

Terpenes contribute in the presence of nitrogen oxides and light to the formation of ground level ozone, radicals, aldehydes, peroxides and other potentially harmful photo-oxidants. Ozone and other photo-oxidants cause forest and crop damage, and are harmful to humans as they cause irritation in the respiratory tract and in sensitive parts of the lungs. The impact of VOC on ozone chemistry is frequently expressed in terms of VOC/NO_x ratios, but the true impact of VOC emissions depends not so much on the total amount of VOC but on the reactivity of the VOC species with respect to OH Sillman [1]. Terpenes are especially reactive and have a large impact relative to their ambient concentration

Terpenes contribute to the forming of aerosols, which contribute to cloud formation (Tunved *et al* [2]), which have an effect on global warming.

1.3 Work environment issues

Exposure limits are set by authorities for monoterpenes and turpentine (a mixture of predominantly monoterpenes, used as solvent). Some examples are given in table 1.

Table 1: Occupational exposure limits for terpenes and turpentine SWEA [3], HSE [4]. TWA=Time Weighted Average.

Country (Body)	Substance	Concentration (ppm)	Concentration (mg/m^3)
UK (HSC)	Turpentine	100 ppm TWA 8 hr 150 ppm TWA 15 min	570 mg/m^3 TWA 8 hr 850 mg/m^3 TWA 15 min
Sweden (SWEA)	Turpentine, monoterpenes	25 ppm TWA 8 hr 50 ppm TWA 15 min	150 mg/m^3 TWA 8 hr 300 mg/m^3 TWA 15 min
USA (OSHA)	Turpentine, α-pinene, β-pinene, 3-carene	100 ppm TWA 8 hr	570 mg/m^3 TWA 8 hr
USA (ACGIH)		20 ppm TWA 8 hr	120 mg/m^3 TWA 8 hr
Norway	Turpentine, 3-carene	25 ppm	150 mg/m^3

2 Anthropogenic terpene emissions

Each step in the processing of trees into products is an opportunity for terpenes to be released. The total emitted amount from a factory's production is the factor most often regulated in permission by authorities to start or increase production. It is therefore of major importance to both regulatory bodies and industry.

2.1 Thinning and logging

The monoterpene concentration in air near the harvester during logging of both Scots Pine and Norway spruce are 1.0–1.5 mg/m^3 (Strömvall and Petersson [5]). Four weeks after thinning, the concentration in air is 50 μg/m^3. This should be compared to the background level of 1–10 μg/m^3.

2.2 Storage

Norway Spruce wood chips in heaps outdoors in a temperature of 12°C emit at most 64 mg terpene/m^3 (Axelsson *et al* [6]). In wood chips the terpene content decrease rapidly, with 4% loss in the first week (Marutzky [7]). Storage of roundwood unsurprisingly causes less terpene emissions than storage of chips. Turpentine yield from Norway spruce and Scot pine has been reported as 23% lower if pulpwood is stored as chips instead of as roundwood (Strömvall and Petersson [26]).

2.3 Barking and sawing

The concentration of monoterpenes in air during single-log barking of Norway Spruce and Scots pine timber are 5–20 mg/m^3, and during drum barking of

pulpwood 50–100 mg/m^3 (Strömvall and Petersson [8]). Measurements in Swedish sawmills have shown terpene concentrations of 50–550 mg/m^3 in air (Lundberg [9]). The higher concentrations were found in older studies before working conditions had received much attention.

Drum barking of Norway spruce cause emissions of 53 g/m^3 produced chips; the average emission for terpenes during sawing of Scots pine was 153 g/m^3 board and for Norway spruce 25 g/m^3 board (Svedberg and Paulsson [10]). With these data, the terpene emissions from a model medium sized sawmill, producing 100 000 m^3 board annually, would be for spruce 1.4 tonnes from barking and 2.5 tonnes from sawing, and for pine 8.3 tonnes from barking and 15.3 tonnes from sawing.

2.4 Drying

Spruce and pine meant for building purposes are generally dried to a moisture content of 18% (dry basis), and for furniture 10–15%.

Norway spruce has a low resin content, as resin is produced by the tree when needed, and thus low terpene emissions when processed. Scots pine produces a constant supply of resin and thus higher terpene emissions. Judging from lumber drying data, the terpene amounts in Scots pine are similar to that of Douglas-fir and Radiata pine.

Table 2: Emissions during drying of boards.

Tree	Max temp (°C)	Monoterpenes (mg/kg odw)	Ref
Douglas-fir	commercial dryer	315	Lavery and Milota [11]
Norway spruce	60–66	<50	Broege *et al* [12]
Ponderosa pine	commercial dryer	1590	Lavery and Milota [13]
Radiata pine	120–140	120–200	McDonald and Wastney [14]
Scots pine	65	210–380	Broege *et al* [12]

Using emission data in table 2, a sawmill drying 100 000 m^3 boards annually in a low temperature dryer would have emissions from the dryer of at most 14 tonnes monoterpenes if the boards are Scots pine, but only 2 tonnes if the boards are Norway spruce.

Fragmented wood is often dried in higher temperatures than boards are. When flue gas is used as drying medium, terpenes will mix with combustion gases, e.g., NO_x. Emissions during commercial drying of sawdust have been measured in exhaust air to 400-800 mg/kg odw (based on Nyrén [15], Münter *et al* [16], Ek *et al* [17]). Using these emission data, a medium sized pellets producer drying sawdust to produce 50 000 tonnes pellets per year, would have emissions from

the dryer of 20–40 tonnes terpenes annually. This estimation from emission data is lower than calculations from terpene content in wood before and after drying. Commercially sawn sawdust tend to have a monoterpene content of about 0.5–4 g/kg odw in its undried state, of which 50–80% are emitted during drying (Ståhl *et al* [18], Marutzky [19]). Using sawdust with 2 g/kg odw would cause about 50-75 tonnes terpenes to be emitted from the sawdust.

The choice of end moisture content and drying technique heavily influence the terpene emissions from the dryer (Ståhl *et al* [18], Granström [20]). Part of the drying gas in Nyrén [15] is recirculated to the burner where terpenes are destroyed.

2.5 Pelleting

Cutter shavings and sawdust of a moisture content of 8–12% (dry basis) are preferred materials for production of wood pellets.

Dry sawdust contain 0.3–1.1 mg/kg odw terpenes, and during the production of pellets, 70–95% is released (Ståhl *et al* [18]). Using these data, pellets production of 50 000 tonnes would emit 10–50 tonnes terpenes, depending on whether the sawdust terpene content are in the lower or higher range.

Peak terpene concentration in the air in two pellet plants using dried sawdust has been measured to 23 mg/m^3 and 15 mg/m^3, respectively, and in one pellet plant using non-dried sawdust to 119 mg/m^3 (Davila [21]). Data of workers personal exposure to monoterpenes range from 0.64 to 28 mg/m^3 (Edman *et al* [22]).

3 Total amount

There are large natural emissions of biogenic volatile hydrocarbons from trees. Boreal forests are dominated by terpene-emitting tree species. Estimates of global natural monoterpene emissions, done after 1990, range from 127 to 147 TgC/yr (Kesselmeier and Staudt [23]). Monoterpene emissions from forests in Europe have been estimated to 3.8 Tg/yr (Simpson *et al* [24]). Emissions from forests in Sweden is about 0.4 Tg/yr (Janson [25]), which can be compared to the anthropogenic emissions from forestry of 0.1 Tg/yr and forest industry of 0.05 Tg/yr (Strömvall and Petersson [26]).

4 Types of terpenes emitted

The terpene amount and composition in trees are different in bark, sapwood, hardwood, and needles or leaves.

4.1 Anthropogenic emissions

Monoterpene emissions from the industrial processing of wood reflect the composition in the wood. The terpene content in Norway spruce wood is dominated by α-pinene, β-pinene and 3-carene (often in an approximate relation

of 3:2:1). The wood has little sesquiterpenes, about 15 mg/kg odw, with longifolene the dominating compound. Bark from Norway spruce has a much higher percentage of myrcene and β-phellandrene (Strömvall and Petersson [8]) than the wood, and about twenty times more sesquiterpenes, mostly β-caryophyllene but also longifolene, α-humulene, α-farnesene, β-farnesene, longipinene, α-cedrene and α-bisabolene (Martin *et al* [27]). In Scots pine wood, α-pinene and 3-carene dominate, followed by β-pinene. Sesquiterpenes in Scots pine wood are mostly muurolenes, with minor amounts of copaene, β-copaene and β-ylangene (Westfelt [28]).

About 20% of the terpenes released during drying of Norway spruce sawdust are sesquiterpenes (Granström [29]).

4.2 Natural emissions

Monoterpene emissions from trees reflect the composition in the needles or leaves. The relative amounts of the monoterpenes in natural emissions from Norway spruce and Scots pine vary widely, though the monoterpenes emissions are usually dominated by α-pinene, β-pinene and 3-carene.

Monoterpenoids and sesquiterpenoids have been identified as major defensive emissions from Norway Spruce foliage, dominated by the oxygenated monoterpene (2)-linalool and the sesquiterpenes α-bisabolene and β-farnesene. Based on precedents in other species, the induced emission of terpenes from Norway spruce foliage may have ecological and physiological significance (Martin *et al* [30]).

5 Discussion

5.1 Work environment

Measurements of terpenes in air regarding workers exposure have focused on monoterpenes. Sesquiterpenes should be measured and added to the total exposure load. This sum of monoterpenes and sesquiterpenes can then be compared to the exposure limit for turpentine. This would be especially important for studies of emissions from bark.

5.2 Emissions from production

Storage of wood chips means considerable evaporation of terpenes. Storage would be a way to lower the terpene content in wood that is to be further processed. However, undried wood chips are susceptible to mould and insect attacks. Storage of dry chips would not have this disadvantage, but there would be emissions during the drying stage.

Estimated emitted amount for barking, sawing and drying of Norway spruce and Scots pine for a model sawmill is shown in table 3. The lower range is for Norway spruce, the higher for Scots pine. The amount actually emitted from

sawdust dryers are similar to the amounts emitted during pellets production, although emissions during drying could be considerably larger as most of the terpenes in undried wood are emitted during the drying process.

Table 3: Monoterpene emissions related to a model sawmill producing 100 000 m^3 board.

Process	Tonnes
Barking	1–8
Sawing	2–15
Lumber drying	2–14

Emissions at the pellets press depend on the amount of terpenes in the sawdust. The variation in terpene content in sawdust used industrially is large, which is important for pellets producers. If a choice is made to reduce emissions at a dryer by terminating drying at higher sawdust moisture content, this high moisture sawdust will increase emissions as the press. It is possible to clean emissions from dryers, for example by returning a part of the exhaust to a boiler. In US, natural gas is used to burn of terpenes from dryer exhaust, but that cause increased NO_x emissions and costs. Pellets presses have less defined exhausts.

5.3 Concentration in air

The concentration of monoterpenes in emission plumes caused by anthropogenic activities is typically 10–1000 times higher than the background level in conifer forests. Comparing this disturbance to herbivory, where 10% damaged foliage will emit about 2 times more monoterpenes, which is sufficient to increase local tropospheric ozone production and suppress local hydroxyl radical concentrations (Litvak *et al* [31]), it is clear that anthropogenic emissions are larger than the natural variation and will alter regional atmospheric chemistry for several weeks.

5.4 Types of terpenes emitted

Sesquiterpenes that are especially active as defensive terpenes are present in Norway spruce bark. Considering that emissions from drying of wood sawdust had a higher proportion of sesquiterpenes than are present in stem wood, drying of bark would likely cause biologically significant emissions of defensive terpenes.

6 Conclusions

Drum barking and pellets factories using non-dried sawdust can cause monoterpene concentrations at or close to the lower occupational exposure limits. Sesquiterpenes should be included in the total terpene exposure load.

Sawing and lumber drying are equally important terpene emitting processes. Emissions during pellets production can be as important as emissions from sawdust drying, although emissions during drying can also be considerably larger depending on drying technique.

The importance of natural versus anthropogenic emissions depends on the environmental issue. Climate change is global. The importance of the terpene contribution depends on the total amount of emitted terpenes. Natural sources of terpenes would therefore be more important than anthropogenic sources. Formation of photo-oxidants is a regional problem. Terpenes contribute in accordance with their concentration. Hence anthropogenic emissions would be more important.. Effects on insects are local, with bark drying an interesting anthropogenic source.

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Measuring fugitive emission in the printing sector as a verification of the solvent management plan according to the EU Solvent Directive

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Abstract

In order to reduce emissions of volatile organic compounds the EU Solvent Directive 99/13/EC sets fugitive emission limits as a percentage of annual solvent input. A solvent management plan is given in annex III, to calculate the fugitive emission value from paper data of solvent inputs and outputs, and to demonstrate compliance. In a project for the Environmental Inspectorate Division of the Flemish Government we measured fugitive emissions at three different sites in the printing sector, all equipped with regenerative incinerators. Several experimental measurement techniques were applied, with the aim of demonstrating the feasibility of checking the reported solvent emissions independently. It was found that in all three cases the fugitive emissions are considerably higher than those reported in the solvent mass balances according to the Directive. The main reasons for the great underestimation are the unfounded assumption of 100% effectiveness of vapour capture by ventilation systems, and the wrong allocation of emission flows to the output terms O1 and O4, which in one case led to a 10-fold lower fugitive emission estimate. We conclude that verification of solvent balance by measurements is necessary to underpin emission reports and national emission data. Our results show that there is a risk that the Solvent Directive is not an effective policy instrument without the proper measurements for verification.
Keywords: Solvent Directive 99/13/EC, solvent management plan, solvent balance, printing, VOC measurement, fugitive emission value, O1 and O4, incinerator.

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1 Introduction

In many industrial processes volatile organic compounds (VOCs) are used, e.g. in the printing and coating sector. This concerns mostly large-scale processes in sectors were the traditional modes of operations cause fugitive VOC emissions. These VOCs in combination with nitrogen oxides (NO_x) largely contribute to the formation of photochemical smog in the sunlit atmosphere through their photochemical degradation pathways Atkinson [1]. In these pathways the formation of ozone occurs. Another characteristic of photochemical processes induced by VOC is the enhanced formation of aerosols Bowman *et al* [2]. In order to prevent or reduce the VOC emissions, the European Community introduced the Solvent Directive in 1999 (EU 99/13/EC [3]).

2 Solvent Directive

Annex IIA of the Solvent Directive sets emission limit values in the waste gases (mg C/Nm³) and fugitive emission limits as a percentage of annual solvent input. The solvent management plan is given in annex III of the Solvent Directive. This plan serves for following purposes:

- the verification of compliance with emission limit values;
- identification of future reduction options;
- enabling of the provision of information on solvent consumption, solvent emissions and compliance with the Directive to the public.

It provides a framework for a mass balance exercise with inputs ($I1$, $I2$) and outputs (O1 to O9) of organic solvents. A brief description of the input and output terms is given in Table 2. The fugitive emission (FE) is calculated by eqn (2). The fugitive emission value (FEV) can be determined directly by eqn (3) or indirectly by eqn (4):

$$FEV(\%) = \frac{100 \times FE}{I1 + I2} \tag{1}$$

$$FE = I1 - O1 - O5 - O6 - O7 - O8 = O2 + O3 + O4 + O9 \tag{2}$$

$$FEV(\%) = \frac{100 \times FE}{I1 + I2} = \frac{100 \times (O2 + O3 + O4 + O9)}{I1 + I2} \tag{3}$$

$$FEV(\%) = \frac{100 \times FE}{I1 + I2} = \frac{100 \times (I1 - O1 - O5 - O6 - O7 - O8)}{I1 + I2} \tag{4}$$

3 Measurements at three plants in the printing sector

In a project for the Environmental Inspectorate Division of the Flemish Government we measured fugitive emissions at three different sites (plants A, B and C) in the printing sector, all equipped with regenerative incinerators. Several experimental measurement techniques were applied, with the aim to demonstrate

the feasibility of checking the reported solvent emissions independently. The reported fugitive emission values are 22% for plant A and 3% for plant C. The inputs of solvents are derived from paper data and the regenerated quantity. The output terms are derived from estimations, emission measurements in ducts and at the outlet of the incinerator and calculations. Plant B has no reported FEV.

The used methods for measuring the VOC emissions are:

- determination of the total ventilation flow of halls by using tracer gas techniques;
- measurements of the solvent concentrations by mobile FID-measurements in workplaces;
- emission measurements in ducts (incl. inlet and outlet of the incinerator) by flow and concentration measurements;
- emission measurements at emission points (doors, windows, ventilation grids, extraction fans, etc) by flow measurements with an anemometer and concentration measurements with a mobile FID and passive samplers.

During the measurement period, the solvent and ink consumption are registered by volumetric and/or mass measurements. Afterwards the solvent balance is filled in for the period of the measurements. The measurement periods are representative for the determination of the FEV.

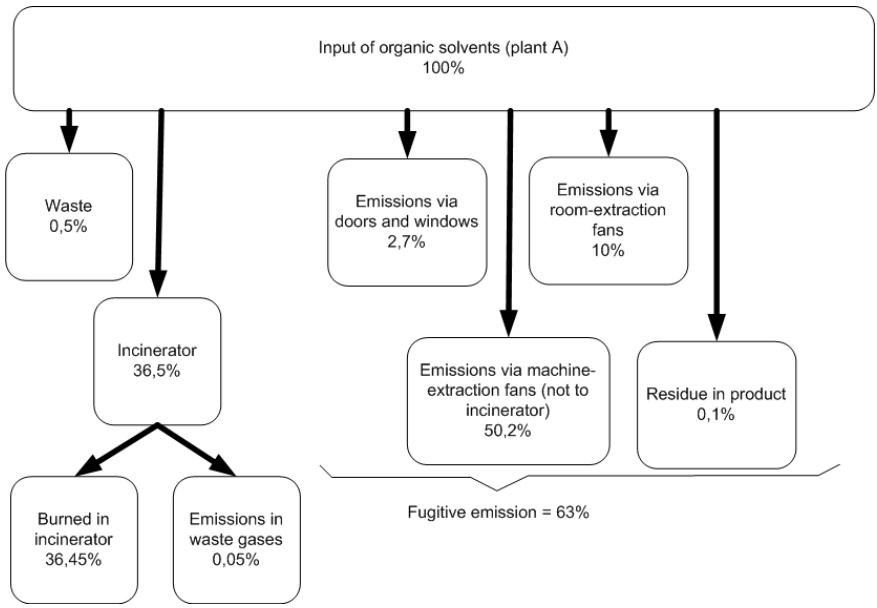

Figure 1: Distribution of the solvents in plant A.

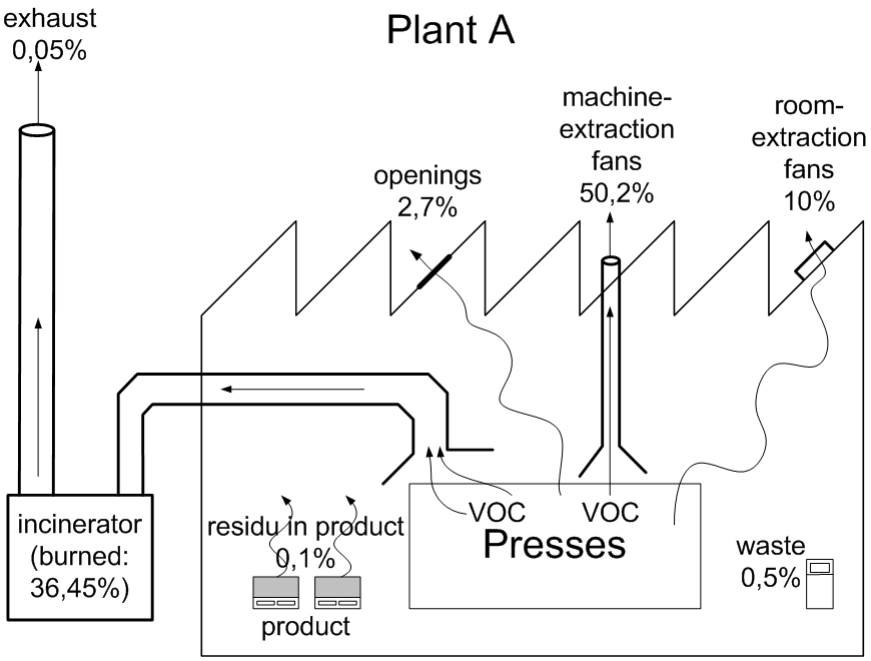

Figure 2: Presentation of the solvent distribution in plant A.

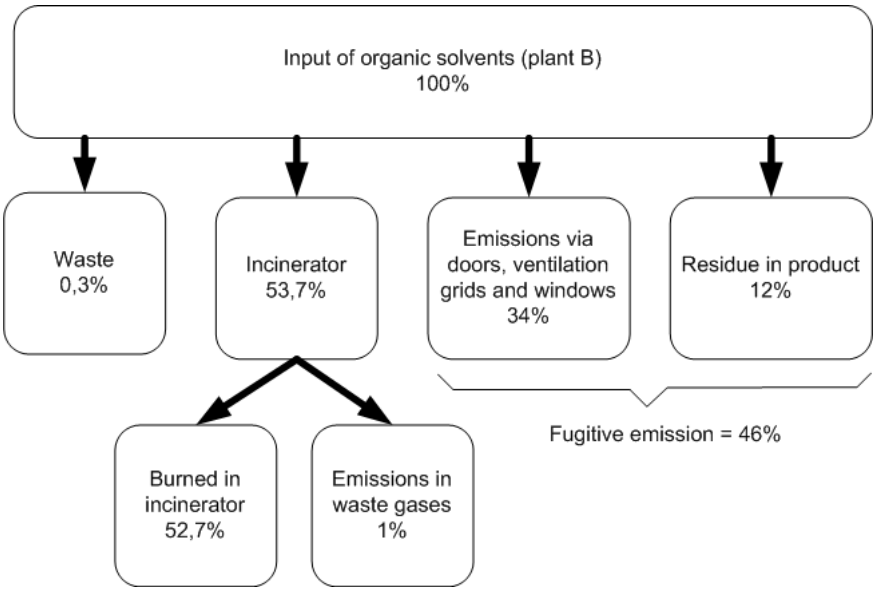

Figure 3: Distribution of the solvents in plant B.

4 Results

4.1 Distribution of the solvents

In all the investigated plants, the solvent consumption (C) finally disappears in the waste and the product, are burned in the incinerator and are emitted via openings/extraction fans. For each plant a summary of the solvent distribution based on the results of the used methods is given in Figures 1, 3 and 4. The VOC emissions of plant A are presented in Figure 2.

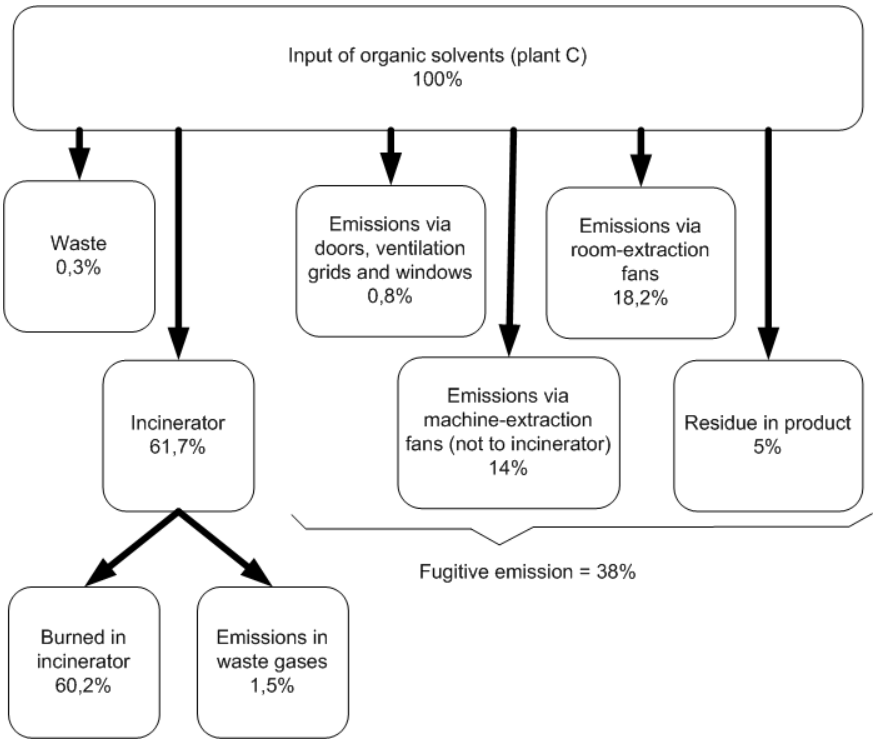

Figure 4: Distribution of the solvents in plant C.

4.2 Emission values

The VOC concentrations in the exhaust of the incinerator are measured for 3 hours and the maximum 1 hour average VOC concentration is calculated. The measured emission concentrations in the exhaust of the incinerators did not exceed the limit emission concentration of 100 mg C/Nm³, Table 1.

Table 1: Emission values in the exhaust of the incinerator.

	emission limit value	plant A	plant B	plant C
max. average emission value of 1h [mg C/Nm³]	100	10	36	59

Table 2: Solvent balances based on measurements.

terms		emission limit value	tonnes carbon/year		
			plant A	plant B	plant C
I1	solvents used as input		1000	100	300
I2	solvents reused		0	0	0
O1	emissions in waste gases		0,50	1	4,5
O2	solvents lost in water		0	0	0
O3	solvent residues in products		1	12	15
O4	uncaptured emissions of solvents into air		629,0	34,0	99,0
O5	solvents lost due to chemical/physical reactions		364,5	52,7	180,6
O6	solvents in waste		5	0,3	0,9
O7	solvents or preparation with solvent sold		0	0	0
O8	solvents in preparations recovered for use		0	0	0
O9	solvents released in other ways		0	0	0
consumption = C = I1 - O8			1000,0	100,0	300,0
fugitive emission = FE = I1-O1-O5-O6-O7-O8 = O2+O3+O4+O9			630,0	46,0	114,0
total emission = FE+O1			630,5	47,0	118,5
			%	%	%
fugitive emission value = FEV = 100*F/I1+I2		20%	63	46	38
relative expanded measurement uncertainty (k=2)			17	14	17
minimum FEV			52	40	32
maximum FEV			74	52	44

For the calculation of the fugitive emission values and the corresponding expanded measurement uncertainties (k = 2), the solvent balances are made, (see Table 2). The fugitive emissions are measured directly with passive samplers, mobile FID-measurements and the flow measurements with an anemometer (term O4). The emissions in the waste gases (term O1) are measured at the outlet of the incinerator. These results are given in Table 2. For the three plants, there are no solvents lost in water, no solvents or preparations of solvents sold and no solvents in preparations recovered for use. Furthermore, there are no other solvent outputs then the terms O1 to O6. So the O2, O7, O8 and O9 terms are not present (terms O2, O7, O8, O9 = 0). The values of the solvent residues in the product (O3) are calculated from the data of the plant (plant A) or from the Dutch guidance document (Verspoor [4]) for plants B and C. The amount of solvents used for washing activities (term O6) are measured.

The FEV are calculated via eqn (3). The calculated FEV for plant A is 63%, for plant B 46% and for plant C 38%. The calculated FEVs of the three plants exceed the fugitive emission limit value by a factor 2 to 3. For each term of the solvent balance the expanded measurement uncertainty (k = 2) is estimated. Finally the measurement uncertainty of the FEV is calculated with GUM-method (ISO guide to the expression of uncertainty in measurement) based on eqn (3). The corresponding (relative) expanded measurement uncertainties for all the calculated fugitive emission values are lower than 20%. Using the expanded measurement uncertainty, the minimum and maximum FEV are calculated, Table 2.

4.3 Rooms at negative pressure?

It was found that in all three cases the fugitive emissions are considerably higher than those reported in the solvent mass balances according to the Directive. The main reasons for the large underestimation are the unfounded assumption of 100% effectiveness of vapour capture by ventilation systems, and the wrong allocation of emission flows to the output terms O1 and O4, which in one case led to a 10-fold lower fugitive emission estimate.

In plant B the VOCs are fugitive emitted via 6 ventilation grids of 2 m² and 2 openings of 4 m² (doors). All the captured gases were led to the incinerator. The plant supposed that there are no fugitive emissions because a negative pressure is maintained in the production hall. Emission measurements at the doors and ventilation grids result in a fugitive emission of 34% of the input via the ventilation grids and the doors. Plant A assumes also that the production halls maintain a negative pressure, but emission measurements results in a fugitive emission of 3% of the input via the ventilation grids and the doors.

4.4 Extraction fans

In plants A and C, most solvent vapours are captured. A part of the vapours is led to the incinerator (terms O1+O5) and the other part is emitted via extraction fans in the environment (part of O4-term), see Figure 1. 99% of the emission that is led to the incinerator is burned. The part emitted via extraction fans is first captured by extraction fans and then released. The definitions of the output terms O1 and O4:

- O1 are emissions of organic solvents in the waste gases.
- O4 are uncaptured emissions of organic solvents to air. This includes the general ventilation of rooms, where air is released to the outside environment via windows, doors, vents and similar openings.

The part emitted via extraction fans is considered as O1 in plants A and C, because they consider this as captured emissions. The gases extracted by the extraction fans are totally released in the environment and finally uncaptured. A part of the extractions fans collects gases from the room and the other part collects gases from the presses.

The fugitive emission value is calculated with eqn (3). A decrease of term O4 in eqn (3), results in a lower FEV. If in plant C the emissions via the extractor

fans are considered as O1, the FEV is 6% in contrast to the 38%. So the FEV is dependent on the interpretation of the O1 and O4 terms. Legally the emissions in the waste gases have to be measured 2 times a year. At plants A and C, the emissions are only measured in the exhaust of the incinerator and not at the extraction fans.

If the emissions of the extraction fans are considered as O1, the VOC concentration limit is 100 mg C/Nm³, but the measured concentrations are usually 1 to 6 times higher. There is a possibility to dilute the VOC concentrations down to concentrations lower then 100 mg C/Nm³ by increasing the flow of the fans or the number of extraction fans. But the amount of VOC emitted to the environment is not decreased by these measures. This could not be an objective of the Solvent Directive. There is the need for a guideline for the allocation of the emissions via extraction fans to O1 or O4.

5 Conclusion

We conclude that verification of solvent balance by measurements is necessary to underpin emission reports and national emission data. Our results show that there is a risk that the Solvent Directive is not an effective policy instrument without the proper measurements for verification. The fugitive emission points are not always known by the plants. Maintaining a hall at negative pressure is not effective in eliminating fugitive emissions.

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Chemical processes effect on ambient air quality: modelling and primary/secondary pollutants monitoring study

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Abstract

The aim of this paper is to show the monitoring results of airborne pollutants around an urban area surrounded with a number of industrial facilities in the state of Kuwait. Data collected (2004-2005) in two different spans included primary and secondary ambient pollutants as well as major metrological conditions. The adsorption effect of PM_{10} on methane gas and other atmospheric chemicals recorded was investigated. A series of concentration and wind roses were constructed to study the prevailing wind and dispersion manner of the airborne chemicals from the different sources. Seasonal analysis was carried out with respect to ground and ambient methane levels from the upstream and downstream neighbouring facilities. A discussion on future strategies for the reduction of the different emitted pollutants from the industrial sites is given.
Keywords: primary pollutants, metrological conditions, downstream, airborne, methane.

1 Introduction

Downstream industry in the state of Kuwait is expanding due to a number of reasons mainly the increase of the local demand on certain crude oil cuts.

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Three refineries process over 1 million BPD are located on the coast line of the urban estate of Kuwait. Applying point source graphing for source determination is paramount to estimate the emissions of pollutants to compute ground level concentrations using dispersion models. The computed model results were synchronized to real time measurements certifying the sources and their respective emission rates. A new approach in estimating elevated source strengths was developed in Pelliccioni and Tirbassi research [1]. The following equation was adapted from the original Gaussian (Normal Distribution) model equation and simulated in a cross wind manner:

$$C(x, y, 0) = C_y\ [exp\text{-}(y^2/2\sigma y^2)] / (2\Pi\sigma y) \quad (1)$$

where; $C(x, y, 0)$ is the pollutant concentration, x is the downwind distance, y the crosswind distance and σy the crosswind spread of the plume

The methodology used was able to improve the error average between the calculated values and the measured ones from 10 different stacks and open tanks. The error decreased from 0.992 to 0.009. In a previous study by Al-Salem et al [2], a series of concentration roses were plotted in a blowing from fashion to monitor the dominate wind and air pollutants on a residential area. The research concluded that the residential area also had excess ambient levels of NOx, CO, H_2S, and ammonia. El-Fadel et al. [3] determined the effects of industrial emissions and the threat a gas like methane can pose to global climate change in the previous decade. An inventory revealed that the industrial sector contributes about 29% to the total greenhouse emissions. They proposed the following correlation to estimate the green house effects of methane gas:

$$Q_i = A\ x\ q_i \quad (2)$$

where; Q_i is the total process emission of gas i in giga grams , A is the production in tons for industrial processes or in Tj for the energy sector and q_i is the emission factor for gas i in giga grams/ton

Health risk assessment using passive samples were analyzed and an annual population risk was calculated due to industrial emissions by Al-Salem and Bouhamrah [4]. Ambient levels of BTEX were studied and an industrial are was divided into three sites to estimate the health effects of PAHs and VOCs.

2 Data collection, materials and software

Locating a receptor point is an essential step in data collection when it comes to air pollution source allocation. The residential area monitored was in the north – northwest of the largest in capacity oil refinery in Kuwait (Mina Al-Ahamdi refinery) and the downwind direction of the greater Burgan oil filed. The receptor point chosen was the main health center of the area (Figure 1.). The data collected in the present work included all the primary metrological conditions data and ambient concentrations of pollutants that included: NOx, SO_2, benzene (C_6H_6), methane (CH_4) and CO. Metrological data included wind speed, wind

direction, percentage relative humidity and ambient temperature. Data were collected in two fashions, original five minute interval data and hourly mean. The main instrument used in the data collection was a fixed five meter probe *(Group TEK. Model)* located on the main health center of the area. EnviDAS software was used to record the pollutants and transform it into EXCEL spreadsheets. Collected data were plotted as concentration roses (CR) using 15° spans of the unfiltered data points. CRs gave an initial feel for the prevailing wind directions and the major sources of the primary pollutants in the area.

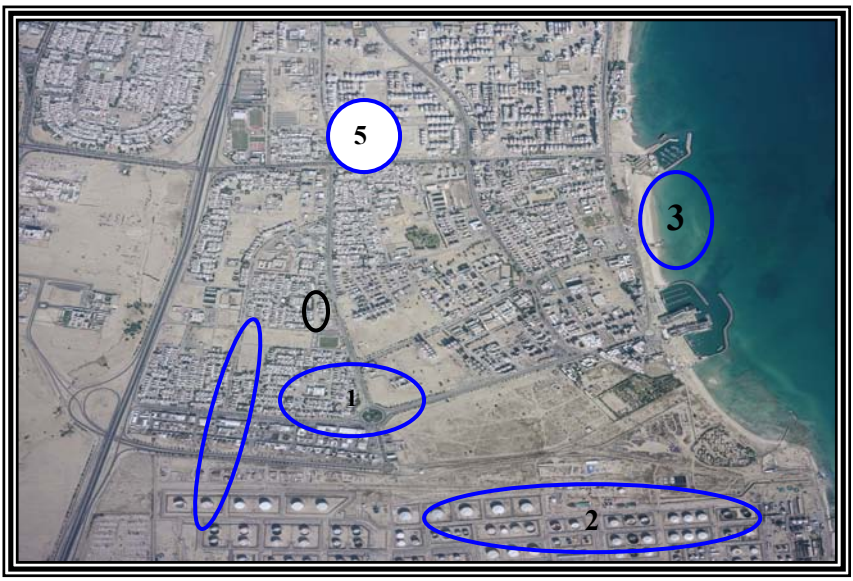

Figure 1: Satellite image of monitored residential area showing the location of the probes used to collect the data (Black circle), and major air pollution sources in the area (blue circles): point 1 shows the main Fahaheel housing area, point 2 shows the MAA refinary gas storage tanks and tank farms, point 3 is the location of the downtown area, point 4 is the Fahaheel main highway and point 5 is Fahaheel sports club.

Figure 2 is an unfiltered concentration rose plotted for the year January 2005, SO_2 was blowing directly from the refinery side. The other industries contribute to the background concentrations of a variety of airborne pollutants. The second dominate source can be detected from the north-north west side which corresponds to Burgan oil filed down winds. Figure 5 shows an unfiltered concentration rose for July 2004. The main source can be determined from the rose as a southern one between 180° to 255°. It can be noticed that methane values are in peaks from the north direction as well, which indicate from the shape of the rose that a number of sources do exist around the area.

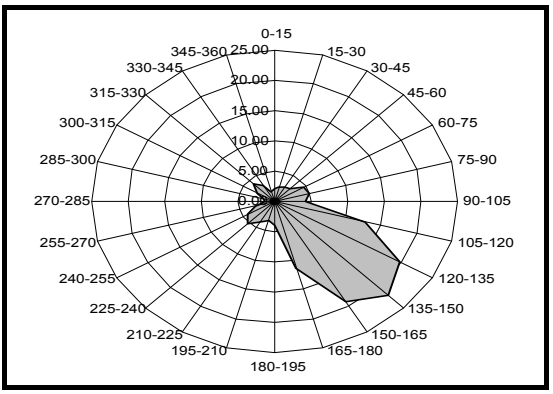

Figure 2: Unfiltered concentration rose for the month of January 2005, SO_2 gas.

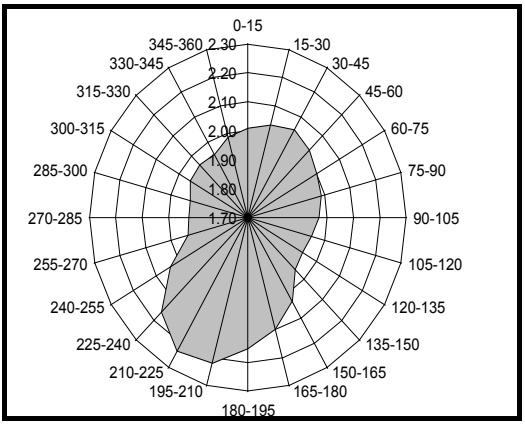

Figure 3: Unfiltered concentration rose for the month of July 2004, methane gas.

Ellipsoid shape CRs were noticed to be in summer periods (July and August) in the area. The prevailing winds in the summer period and their high velocities dispense the gas more than the cooler times. The dot shape CR can be noticed in periods of temperatures below 30°C (Figure 4.), were the ellipsoid like shape can be noticed in a climate of temperatures around 38°C and exceeding. The original data collected was filtered using the OX relation of ambient accumulative concentration levels [5, 6]. Filtered data came to 3% of the collected original data.

The series of CRs constructed concluded that the main methane source that highly contributes to the receptor point is blowing directly from the MAA refinery side many sources can be noticed but none are as highly noticeable as the MAA refinery side one, were methane gas (in all the 19 months data) was

blowing from that side in continues manner with increasing rates. The refinery side occupies the southeastern and western border of the area, making it impossible not to notice the effect and emission rates of methane gas in the monitoring station.

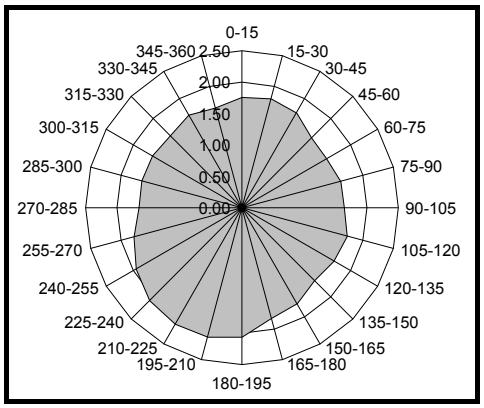

Figure 4: Unfiltered concentration rose for September 2004, methane gas.

3 Modelling step

Filtered data points were thoroughly investigated to model the area under investigation. An adaptation of the Guassian (Normal Distrubution) model was used in this study to estimate the major source of methane emmision. Chemical and physical nature of effluents are considered to be very important in terms of choosing the Gaussian model. Estimating a point's concentration for an elevated source can be done using the traditional Gaussian (Normal Distribution) model equation known. Minor assumptions are made to fit the model to our case. Equation (3) expresses the traditional Gaussian equation used to estimate the concentrations in an elevated source level, adding the reflection contribution term. Researchers estimate the reflection distance to be double the stack or source height.

$$C(x,y,z) = (Q / (2\Pi u\sigma_z\sigma_y)) [exp - (y^2 / (2\sigma_y^2))] [exp (-(z-H)^2/(2\sigma_z^2)) + exp(-(z+H)^2/(2\sigma_z^2))] \quad (3)$$

where, $C(x,y,z)$ is the concentration of a certain airborne pollutant with respect to the three coordinates, Q is the emission strength of the source in (mass/time), H is the source effective height estimated as $H = h + \Delta h$, where h is the true height of the source and Δh is the plume rise all in meters, u is the wind speed in m/s), z is the receptor point elevation in meters, x, y and z are the coordinates

from the imaginary axis drawn with respect to the wind direction, σ_y and σ_z are the dispersion coefficients with units of meters or Kilometers. The calculations in this study are based on the stability **class C** and its conditions since it is the most reported one in the state of Kuwait [7]. The two dispersion coefficients were either estimated in graphical means or better yet calculated from fitted linear correlations. Both dispersion coefficients were evaluated from Wark [8].

The methane concentration and conditions used to model the dispersion manner for the point source followed Table 1 in terms of the points used to calculate the emissions of the MAA refinery. The month of July 2004 was chosen since methane recorded high activities along the month. The value in the table corresponded to the Southeast direction (169°-Refinery side) with respect to the maximum concentration of methane at that time. A few assumptions were made regarding the modeling of our point source. First, the downwind direction (Southeast) was considered to be the only wind at the time of measuring, thus corresponding to the imaginary axis drawn. The second assumption was considering the source in the refinery (Tank farm/South side) half full at all times; giving an elevation of 10 m. This means no effective stack height is calculated, taking H equals to 10 m at all times. This is very important to be careful when choosing the Gaussian model. The downwind direction was chosen as the imaginary axis. Figure 4 show the imaginary axis scale with respect to the point source and the receptor point.

Table 1: Recorded methane conditions used in estimating the emissions of the refinery as a point source.

Day	Date	Week	Peak time	Peak Value (ppm)	Wind direction (deg)	Temp. (°C)	Humidity %	u (m/s)
Monday	19th	3	8:00 pm	3.33	169	40.2	36	4

The distance between the receptor point and the source in the refinery was 14.5 cm on the paper scale, which corresponds to 2230.5 m (2.2 km) in real distance with respect to the scale of the image. The concentration of methane was taken as 3.33 ppm which converts to 2.174 mg/m^3. The dispersion coefficients y and z were calculated to be respectively 29.858 km and 127.323 km. The Q value was calculated to be 1.04 gm/s. This calculated number gave the value of methane being emitted from the point source to Fahaheel area. The objective was to calculate the rate of methane being emitted from the whole refinery side. The refinery area is reported to be 10,533,400 m^2, and by dividing by that number the rate of methane being emitted is found to be equal to 10 gm/(m^2.s). Taking a plus or minus one percent for unaccounted emissions or conditions. Of course the main methane sources in MAA refinery were mentioned once before as tank farms, LPG units, and gas gathering centers. In addition to, cracking units and the gas pipe lines.

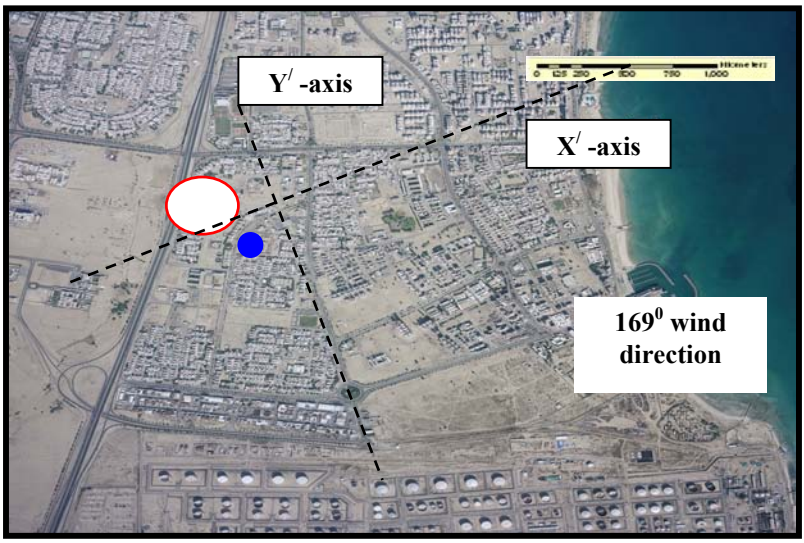

Figure 4: Imaginary axis lines for point source modeling, the corresponding coordinates were: x = 14.5 cm and y = 2.1 cm. The blue dot represents the source at the refinery (Tank farm) and the red circle represents the receptor point.

Table 2: Concentration profile values obtained from Equation (6).

x imaginary (cm)	x real (m)	σ_y (km)	σ_z (km)	C (mg/m^3)
14.5	2230.769	29.8	127.36	2.03
14	2153.846	28.75	123.3	2.169
13	1999.99	26.53	115.25	2.48
12	1846.153	24.32	107.22	2.87
11	1692.307	22.12	98.92	3.34
10	1538.46	19.98	90.66	3.93
9	1384.46	17.79	82.33	4.68
8	1230.76	15.66	73.92	5.26
5	769.23	9.4	48.09	9.5
4	615	7.37	39.21	9.96
3	307.692	5.3	30.1	7.2
2.5	384.61	4.4	25.5	4.14
2	307.692	3.43	20.8	1.1

4 Results and discussion

The Gaussian model dealt with the strength of the primary source rather than its contribution. After calculating the strength of the source, the concentration profile was developed in order to asses the touch down point in the investigated

area. Equation 4 is the obtained equation (Concentration profile) that resulted from plugging the obtained source strength Q in the Gaussian equation. Table 2 show the calculated concentrations from the formulation got from the model.

$$C(x,y,z) = (1.04\ gm/s / (2\Pi (4\ m/s)\ \sigma_z\sigma_y)) [\exp - (y^2 / (2\sigma_y^2))] \times [\exp(-(z\ H)^2/(2\sigma_z^2)) + \exp((z+H)^2/(2\sigma_z^2))] \quad (4)$$

The values tabulated above are the basis of the Gaussian (Normal Distribution) graph that will be discussed in the upcoming section. The modification came in excluding the effective height and using the half full height at the tank farm. The refinery side gave a 2 ngm/s.m^2 NO_2 emission rate or strength (MAA refinery total area = 10533400 m^2), taking in perspective the total area of the refinery. Methane is known to be one of many existing hydrocarbons in the atmosphere were it can disperse and be absorbed like any other gas. Over the course of this study, it was noticed that methane had an opposite trend with the dust levels in the ambient. Dusty seasons are known in Kuwait to be summer and beginning of the autumn. Dust means in micrograms/m^3 and methane mean values in ppm are tabulated in Table 3.

Table 3: Methane and dust mean averages.

MONTH	METHANE MEAN (ppm)	DUST MEAN (ug/m^3)
APRIL04	2.06	120.65
MAY04	2.05	446.29
JUNE04	1.97	177.82
JULY04	2.02	167.77
AUGUST04	1.92	132.00
SEP04	1.74	167.00
NOV04	2.05	264.00
DEC04	1.97	378
JAN05	1.81	143
FEB05	1.92	199

It is clear that dust levels based on monthly means reached in the filtered data points up to 446 micrograms/m^3 in the beginning of the summer season of year 2004. Wind speed is in a direct relation with the dust levels in the ambient. Summer seasons are always associated with high wind velocities. Figure 5 is a graph constructed to plot dust levels with methane ones against time periods in monthly durations. It is noticeable from the figure that dust levels increase in hot periods in Kuwait and methane levels are minimum with high dust levels. This effect is known as “Dust adsorption” of methane in the ambient [11]. Methane levels vary from month to month. The cooler periods help methane settle in the atmosphere and suspend for a longer period in the lower layer of the ambient air. Severe metrological conditions like high wind velocities help dispense methane gas and make it scarce in the surrounding outdoors. July is always a good representative of summer periods in Kuwait. Figure 5 is the stock graph of the month of July 2004, with minimum, maximum and mean values of every day of the month present on it. Almost all of the methane mean values correspond to a lower mean of dust recorded. In plotting the normal distribution

concentration profile that was developed (Table 2) one can develop the regular dome shape of the normal distribution model. Figure 6 is the one developed for this purpose were the touch down point is circled and found out to be at x imaginary equals to 10.02 cm which corresponds to 1541 meters from the MAA refinery which is exactly on the main housing area of the urban estate studied.

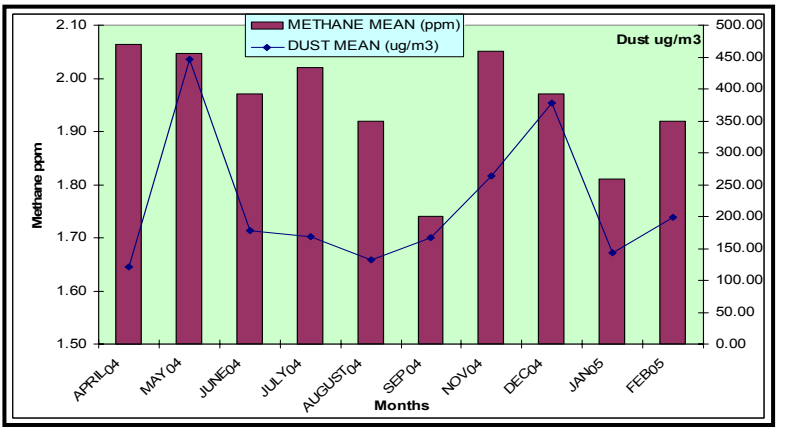

Figure 5: Dust and methane levels plotted against months.

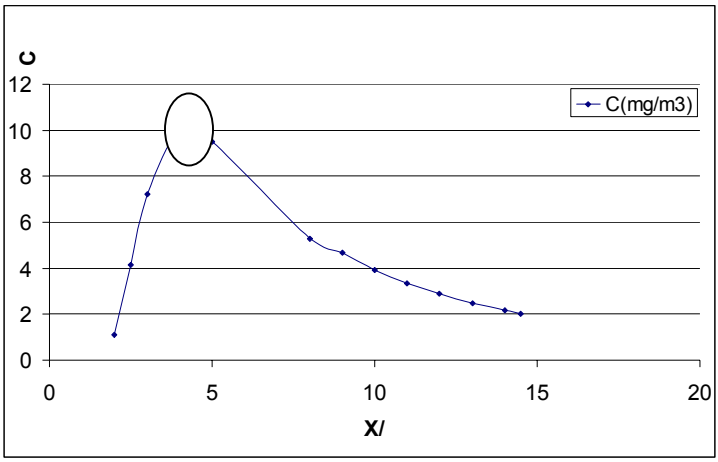

Figure 6: Normal distribution of methane gas over studied area.

5 Conclusion

With the use of the Gaussian model, a residential area was modeled and the strength of the main source of methane was determined. The adsorption effect of dust suspended in the atmosphere was detected in the area. A number of primary

and secondary pollutants all resulting from refining, petrochemical and cottage facilities were monitored. Concentration roses of a number of airborne chemicals were executed in order to determine the dominate sources surrounding the urban estate. Rules and regulation of KUEPA must be strictly applied and regular check ups are mandatory at this stage.

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Air quality in vicinity of a government school in Kuwait

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Abstract

There is a growing concern in Kuwait for the air quality in the vicinity of schools. The problem is exacerbated at peak times of congestion, which adversely affects the traffic flow and air quality. Several primary pollutants have been observed to be excessive during the peak periods in the country.

Air quality in the vicinity of a government school was assessed in March 2006 for a period of two weeks using an air pollution monitoring station, which continuously recorded various pollutants' concentrations and meteorological variables at five-minute intervals. The results show that during the weekdays, the measured pollutants emitted from the road traffic next to the selected school, such as carbon monoxide (CO) and nitrogen dioxide (NO_2), were always under the allowable limits for Kuwaiti air quality standards, except for a single occurrence of increased NO_2 concentration at morning hours. On the other hand, the values of non-methane hydrocarbon pollutants were found to be several times above the Kuwaiti air quality standards throughout the investigated period. The suspended particulates (PM_{10}) concentrations have twice exceeded the limits of Kuwaiti air quality standards. A traffic counter was used to record the number of cars in the main road next to the school in fifteen-minute intervals for ten days during the monitoring period for air quality. Statistical analysis was used in order to test whether there is any correlation between variations in the CO concentrations and the traffic frequency during working days' morning and afternoon periods. A relation was developed for predicting the necessary reduction in traffic based on the necessary reduction in CO concentrations.
Keywords: congestion, pollutants, correlation.

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1 Introduction

In Kuwait, the urban population is growing at about 3.4% per year [1]. This increase in population in addition to the development of urban areas has in turn resulted in massive increase in the demand for transport. Motor vehicles and buses are the only means of road transportation in Kuwait. Road vehicles have increased as shown in Figure 1 with an average growth of 3.0% annually. The number of buses has not increased from year 1993 until year 2002 [2], and its annual growth rate is negligible. At present, there are 377.2 vehicles for every 1000 persons, which indicate that there are 2.65 persons per car [1]. Motor vehicles and buses cause environmental pollution due to exhaust emissions and tyres abrasion which depend on driving cycles, engine design and condition, fuel composition and air to fuel ratio. The vehicular emissions constitute harmful pollutants that affect the health adversely such as carbon monoxide, particulate matter, nitrogen oxides, and lead. A large proportion of urban pollution is mainly due to road traffic.

According to the Ministry of Education (MOE) in Kuwait statistical data and Ministry of Planning statistics, the school buses are serving approximately 17 to 18% of students in the government schools. Based on 2003/2004 statistics, there are 23,302 students using buses out of 131,597 total students. The rest of students mostly depend on private transportation.

According to various reports [3], it was proved medically that the vehicle air pollutants such as nitrogen dioxide (NO_2), carbon monoxide (CO) and particulates (PM10) have pronounced effect on human health as shown in Table 1.

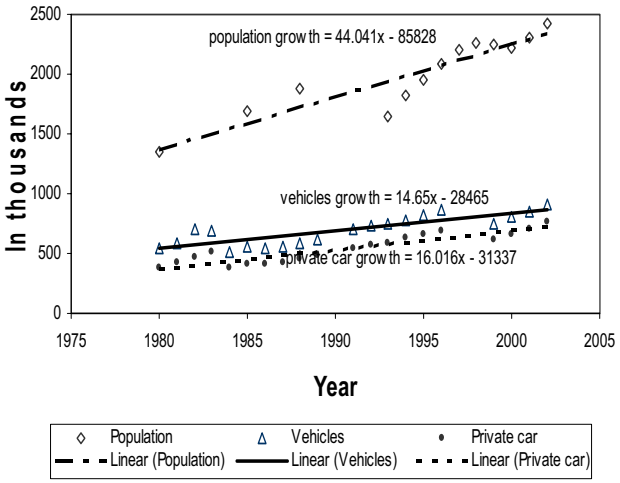

Figure 1: Vehicles in use and the growth of population [1].

Table 1: Health effects of vehicle air pollution.

Pollutant	Source	Health Effects
Nitrogen dioxide (NO_2)	One of the nitrogen oxides emitted in vehicle exhaust	May exacerbate asthma and possibly increase susceptibility to infections
Particulates PM_{10}, Total Suspended Particulates, Black smoke	Includes a wide range of solid and liquid particles in air. Those less than 10μm in diameter (PM_{10}) penetrate the lung fairly efficiently and are most hazardous to health. Diesel vehicles produce proportionally more particulates than petrol vehicles	Associated with a wide range of respiratory symptoms. Long-term exposure is associated with an increased risk of death from heart and lung disease. Particulates can carry carcinogenic materials into the lungs
Carbon monoxide (CO)	It is mainly produced from petrol car exhausts	Lethal at high doses. At low doses can impair concentration and neuro-behavioral function. Increases the likelihood of exercise related heart pain in people with coronary heart disease. May present a risk to the fetus
Ozone (O^3)	Secondary pollutant produced from nitrogen dioxides and volatile organic compounds in the air	Irritates the eyes and air passages. Increases the sensitivity of the airways
Volatile organic compounds (VOCs)	A group of chemicals emitted from the evaporation of solvents and distribution of petrol fuel. Also present in vehicle exhaust	Benzene has given most cause for concern in this group of chemicals. It is a cancer causing agent which can cause leukemia at higher doses than are present in the normal environment

Source: [3].

2 Study area

The government school, which was selected for the study, is located at Mishref Area in a flat and homogeneous terrain region without any major local air pollution sources. This school is surrounded by Road 57 from the north, as shown in Figure 2 [4], which is considered a main street, and from the east there is another school under construction. From west and south there are minor streets. The school is surrounded by residential houses and other governmental schools. The schools are adjacent to each other in one lane and there are no school buses in the mornings or afternoons for students.

The school area is 18,000 m² and has parking at the front of the school entrance gate. About 985 students attended this school for year 2005/2006 during the time of monitoring the air quality.

Figure 2: Location of the governmental school at Mishref area.

3 Methodology

Air quality and weather data were recorded at sampling intervals of 5 minutes by the Kuwait Institute for Scientific Research (KISR) air monitoring station, as shown in Figure 3, for two weeks. The measured data included the concentration of different pollutants such as carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and non-methane hydrocarbons, nitrogen oxides (NO_x), nitrogen dioxide NO_2, and suspended particulates (PM_{10}). In addition, the measured data included wind speed, wind direction, solar radiation and ambient temperature. The monitoring station was parked in the Mishref area next to the governmental school entrance. A traffic counter was used to record the number of cars in the roads, as shown in Figure 4, next to the selected school for every 15 minutes

throughout the study period. The measurements were taken in March 2006 including weekdays and weekend holidays. Statistical analysis of the recorded data was performed to establish whether there is any correlation between working days' variations in the levels of CO and the traffic frequency in the vicinity of the government school.

Figure 3: Air monitoring station next to school.

Figure 4: Car counters on the selected road.

4 Discussion and results

4.1 Traffic

The hourly average weekday and weekend traffic flow profile is shown in Figure 5. The profile of the traffic indicates two peaks during the working days which are related to the opening time of the school and start of working hours in the morning and closing time in the afternoon and end of working hours. At weekends there are no sharp peaks and traffic flow gradually increases followed by slight decrease at afternoon time then minor increase in the evening.

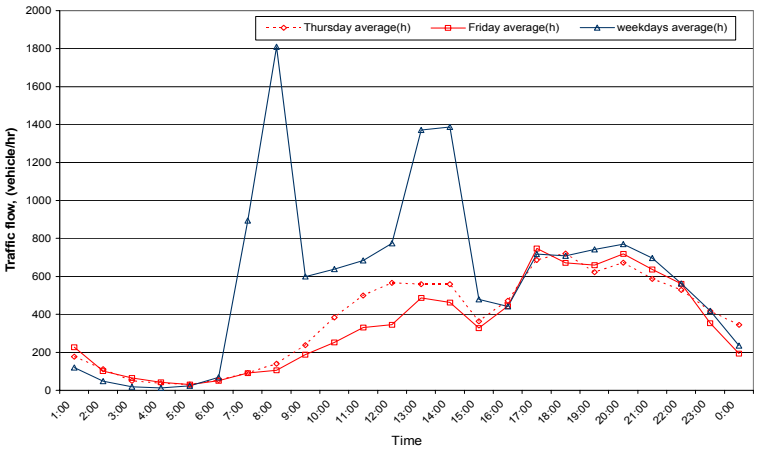

Figure 5: Hourly traffic flow for weekdays and weekend days at the site.

4.2 Air quality

All the measured pollutants' concentrations in the vicinity of the selected school for a period of two weeks were compared with the allowable levels according to Kuwait's air quality standards. The Air Quality Standards (A.A.Q) in the residential areas for Kuwait, Federal US and California states are presented in Table 2. The mean concentration and the maximum and minimum level of CO, NO_2, and PM_{10} pollutants are shown in Figures 6 to 8. The CO concentrations are always under the allowable limits. The average non-CH_4 concentrations are always above the specified limits as shown in Figure 9. NO_2 concentration had exceeded the allowable limits 15 times during the study period. The NO_2 exceedances are mainly due to road traffic since these values were associated with the increase of CO levels. Regarding PM_{10} levels it has exceeded the limits of A.A.Q (on two occassions) during the time of recording.

Table 2: The Hourly Air Quality Standards for Kuwait, Federal US and California state.

Pollutant	Kuwaiti Standard*	Federal Standard	California State standard
Ozone µg/m^3	157	235	180
CO (ppm)	30	35	20
NO2 (ppm)	0.1	-	0.25
PM10 µg/m^3	350 (24 hours)	150 (24 hours)	50 (24 hours)
Non methane HC	0.24 ppm for a period of 3 hours (6-9 AM)	-	-

Source: [5].

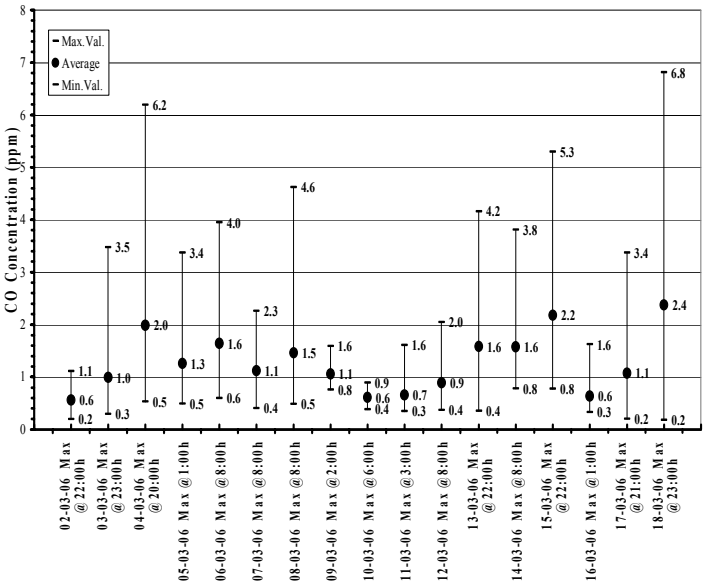

Figure 6: Mean, maximum, and minimum level of CO concentrations.

4.3 Statistical analysis

The recorded data for CO concentration and cars counts on every 15 minutes during the study period were analyzed taking into consideration the morning hours from 5:00hr -10:00hr and afternoon hours from 11:00hr -16:00hr. This strategy was adopted in order to decrease the influence of traffic in the surrounding area and to focus mainly on the traffic in the vicinity of the school, which is the main objective of this research. For the selected time periods, the measured CO concentrations are plotted against car counts for the 15 minutes intervals. A strong correlation is found in mornings showing 4.4 ppb car while in the afternoon the CO emissions were 1.3 ppb car depending on the traffic flow as shown in Figure 10. The dispersion of pollutants is slower in morning times than afternoon due to prevailing meteorological conditions, temperature, wind, and inversion layer. The equation, which was obtained from the morning trend of cars versus CO concentration, was used to predict the effect of reducing the number of cars according to the desired level of CO concentrations. Figure 11 presents the dependency of CO concentration reduction as a function decrease in number of cars on the road in the vicinity of the school. This correlation is very important and can be used to regulate the traffic according to desired reduction in air pollution. In this case 40% reduction in traffic leads to 32% reduction in CO concentration.

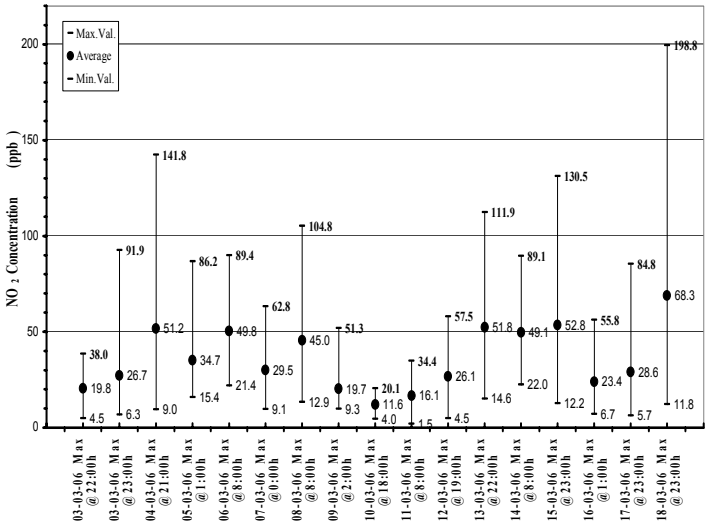

Figure 7: Mean, maximum, and minimum level of NO_2 concentrations.

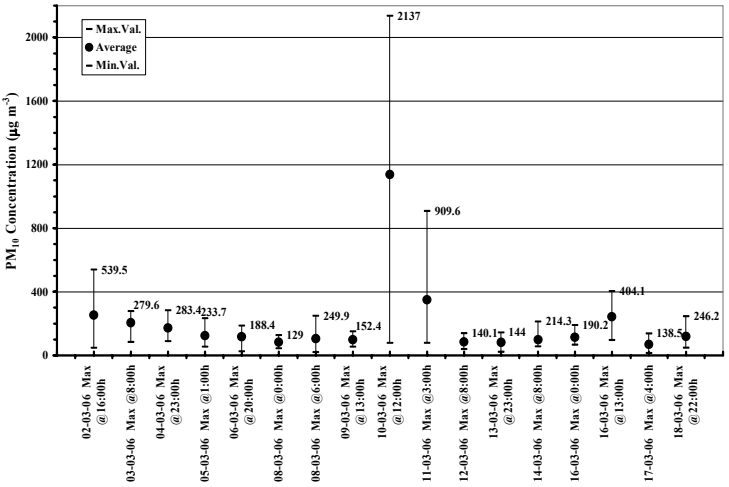

Figure 8: Mean, maximum, and minimum level of PM10 concentrations.

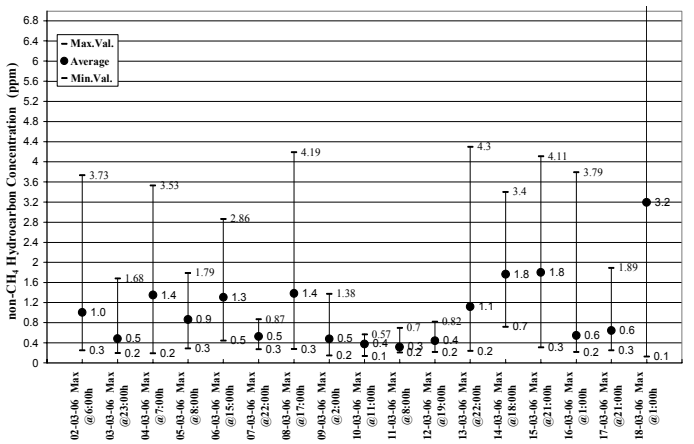

Figure 9: Mean, maximum, and minimum level of non-CH_4 Hydrocarbon concentrations.

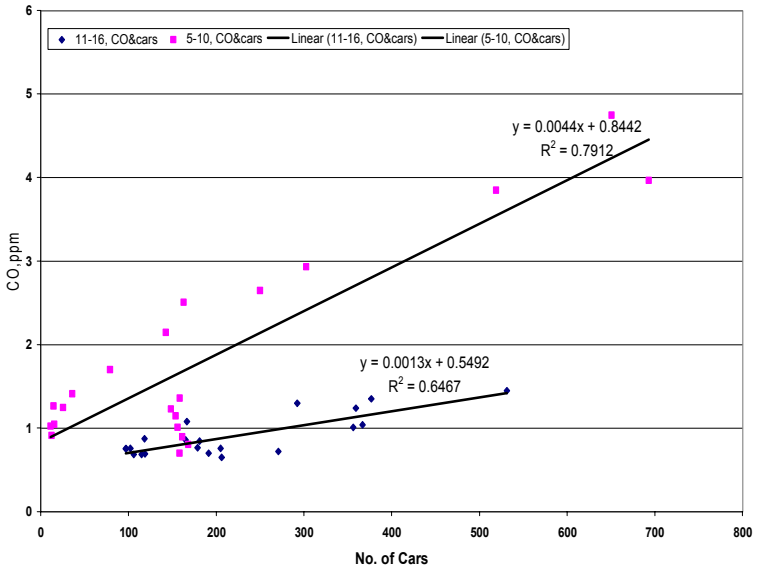

Figure 10: The correlation between CO pollutant and the number of cars (5 – 10 = morning hours; 11 – 16 = afternoon hours).

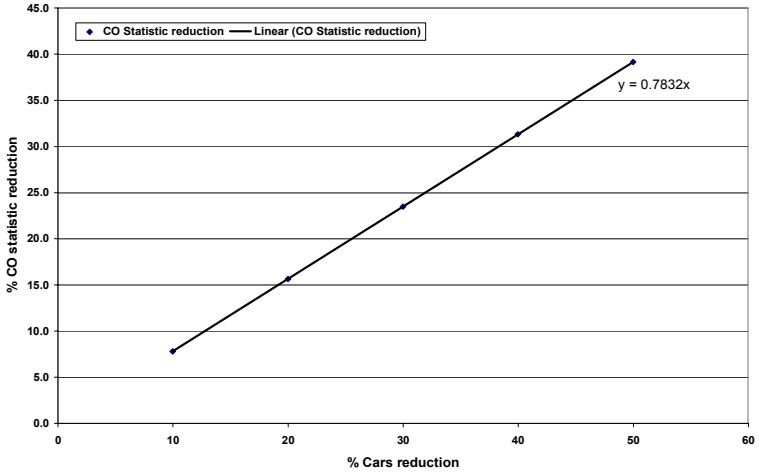

Figure 11: The predicted effect of decreasing the number of cars on CO concentration.

5 Conclusion and recommendation

It is important to maintain high standards of air quality around the schools in order to reduce the effect of traffic pollutants on health of children and their performance. High levels of pollution and traffic conjunctions are recognized as health risk.

The Kuwait government should consider public transportation for the governmental schools students to abate traffic conjunction and associated air pollution problems in the country.

Protective measures such as introduction of school buses using superior quality fuel to combat high pollutants emissions are required to achieve good ambient air quality in the country.

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Mapping anthropogenic B(a)P releases in the Great Lakes Basin

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Abstract

Benzo(a)pyrene (BaP) is one of the most toxic PAHs. It is listed as a priority toxic substance with a target for virtual elimination under the Great Lakes Bi-national Toxics Strategy (GLBTS). At the GLBTS's meeting in December 2005, BaP monitoring data of both Canada and U.S.A. shows that ambient BaP concentrations at urban sites are 10 times higher than those in rural sites, reflecting a significant local source contribution. This paper is prepared to (1) Map the local releases in nine province/states of the Great Lakes Basin (2) Analyze sources of BaP in high-releasing regions (3) Map ambient air monitoring data in the Basin. The BaP inventories used for the mapping originated from USEPA's 1999 National Emissions Inventory (NEI) and Environment Canada's Ontario inventory 2003. Approximately 27,000 kg of BaP releasing from the Basin's anthropogenic sources were mapped, with 30% from Ontario, Canada and 70% from the eight states in the U.S. The Basin is divided into 280 grid cells (each 100 km x 100 km) using a high-resolution GIS mapping tool. It is found that five grid cells with releases in 1,000–2,000 kg/year are the highest relative to the others in 10–1,000 kg/y. They are located in Ontario, Ohio, Illinois, and Indiana. This agrees well with the higher ambient BaP concentrations detected in the Chicago, Hamilton, and Toronto areas in these province/states in the past 15 years. The 2003 annual averages were 500, 300, 200 pg/m^3 for these three cities, respectively. The common source sectors of BaP in both countries are steel manufacturing, residential wood combustion, scrap tire burning, the use of creosote railway ties, primary metals production, household waste burning, and motor vehicles.

Keywords: Policyclic Aromatic Hydrocarbons (PAHs), Benzo(a)pyrene (BaP), Great Lakes Binational Toxics Strategy (GLBTS), emission inventory, Great Lakes Basin, mapping, release, ambient air monitoring.

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1 Introduction

The paper is prepared to improve the understanding of BaP releases to the environment and to address some issues raised by the BaP management assessment of the Great Lakes Binational Toxics Strategy (GLBTS) [1]. This paper maps annual BaP releases from each county/municipality in nine states/province, which locates the BaP high-releasing areas and the ambient air concentrations in the GL Basin. The information is useful in identifying locations and specific sources to help take actions towards BaP reduction and ambient air quality improvement.

High-resolution GIS mapping tools are used to map annual release of BaP in the GL Basin in 2003. Majority of BaP was released to air with few to soil, and water. The 1999 NEI data were directly provided by USEPA [2]. The Ontario 2003 inventory is developed by Environment Canada that is used to support the GLBTS [3]. The U.S. and Ontario data are reviewed to ensure the source sectors are comparable, but the estimation methodologies for each source sector are not reviewed. Due to the unavailability of the 2003 NEI data at the time of this mapping work was undertaken, it is assumed 1999 NEI inventory reflects the level of BaP releases in 2003 in the U.S. states.

2 The Great Lakes Basin: area and population

The GL Basin includes the five Great Lakes, the eight states of U.S.A. and Ontario province of Canada. The area and population of each state/province is summarized in Figures 1 and 2. The area size of Ontario (1,076,395 km^2) in Canada is as large as the total of the eight states (1,073,815 km^2), while Ontario population (12,256,645) is only 15% of the total of the eight states in the U.S.A (82,892,648).

Figure 1: Nine States/Province and Five Great Lakes in the Great Lakes Basin.

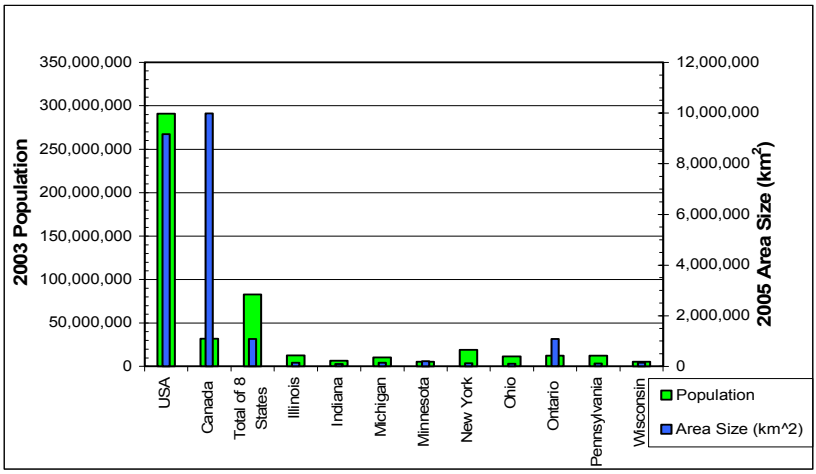

Figure 2: 2003 Population and 2005 area size of the Great Lakes States/Province [4,5].

3 BaP Releases in the Great Lakes Basin

The 2003 BaP releases are plotted in Figure 3. 8,400 kg and 18,500 kg of BaP were released from Ontario and the eight states respectively, which makes a total release of 27,000 kg to air, soil, and water Basin-widely with majority to the air. The contributions from each source sector in Ontario of Canada and the eight states of U.S. are described separately below.

For the 2003 Ontario BaP inventory of 8,400 kg, the population and spacial intensity is 0.6 g/capita/year or 8 g/km^2/yr. 65% came from non-point sources, 25% from point sources, and 10% from mobile sources. The major source sectors are the use of creosote railway tie (30%), residential wood combustion (28%), iron & steel sector (25%), and motor vehicles (10%) [3].

For the 18,500 kg of BaP in the eight states of the U.S.A., the population and spacial intensity is 0.2 g/capita/year or 17 g/km^2/yr. They were released from a few source sectors including household waste burning (HWB), open burning-scrap tire (OB-ST), residential wood combustion (RWC), Iron & Steel (IS), petroleum refining (PR), primary non-ferrous metals (PNM), health service (HS), ferrous foundries (FF), diesel motor vehicles (DMV), and gasoline motor vehicles (GMV). 65% came from non-point sources, 29% from point sources, 4% from on-road and 2% from non-road mobile sources. The major source sectors are residential wood combustion (30%), household waste burning (15%), open burning-scrap tires (10%), primary non-ferrous metals (8%), iron & steel sector (6%), and motor vehicles (4%) [6].

The releases from non-point and point sources are significant in both countries with non-point source is twice as high. It is worthy to note that the Ontario estimates on non-point source and on-road mobile source are all

substantially greater than those in any of the U.S. states. The difference in Ontario estimate points to a possibility in the difference of the estimation methodologies of both inventories. In addition to the benefit on identifying high-releasing areas and their source sectors, this paper helps to highlight some data gaps on the inventory development

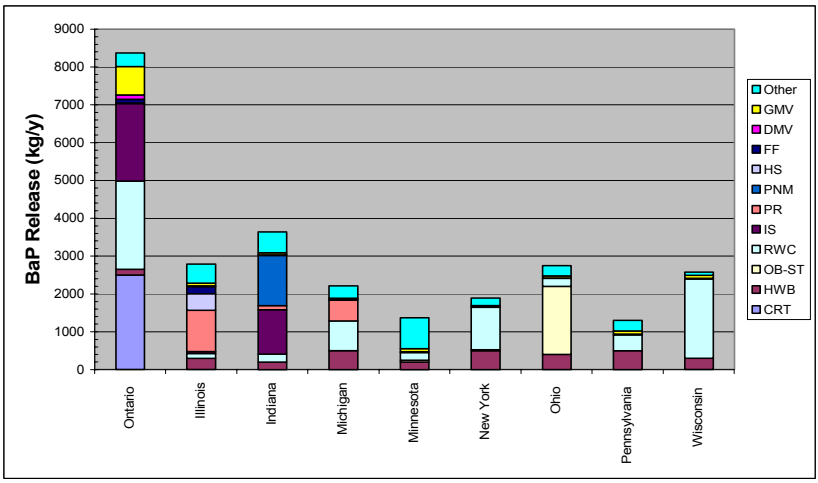

Figure 3: Releases from major source sectors in each State/Province.

4 Mapping BaP releases in the GL Basin

27,000 kg of BaP releases from each counties and municipalities are mapped on a digital map. The Basin is divided into 277 grid cells (164 cells in U.S. and 113 cells in Ontario). B(a)P releases in most grid cells range from 10 to 1,000 kg/yr, refer to Figure 4. However, there are five grid cells (four of them in U.S.) have higher releases in 1,000-2,100 kg/yr from Iron & Steel, Primary Nonferrous Metals, Petroleum Refining, Scrap Tire Burning, and Petroleum Refining. The findings are consistent with those from the county-based map (not shown). These cells are located in Toronto/Hamilton area in Ontario, Columbus area in Ohio, Chicago area in Illinois, and the other two cells located in Indiana and Illinois that are further away from the Great Lakes, see Table 1.

5 Mapping ambient air BaP in the Great Lakes Basin

The monitoring data from International Air Deposition Network (IADN) and National Air Pollution Surveillance (NAPS) are used to compare with the local releases of BaP. It is found that the ambient air BaP is higher in the area with higher BaP releases, such as in urban cities.

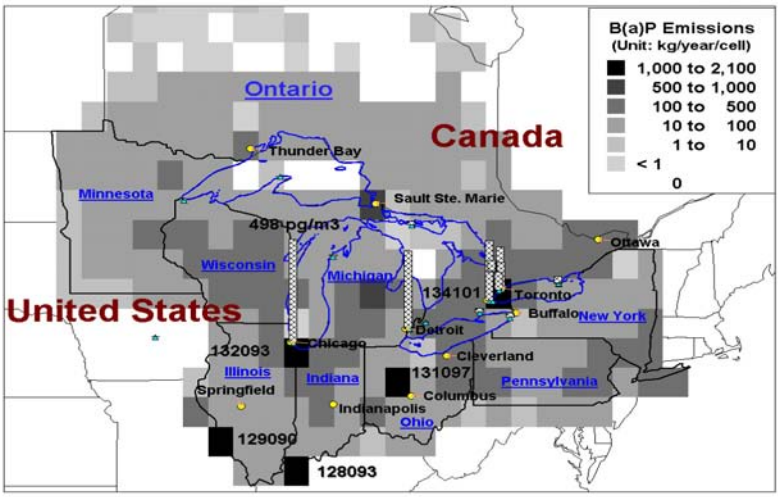

Figure 4: Gridded B(a)P Emissions in the USA (1999) and Ontario Releases (2003).

Table 1: Five grid cells with highest BaP releases in the Great Lakes Basin.

Grid Cell (GEIA)	BaP Releases (kg/yr)	Major Sources	Major City	State/Province
134101	2040	Iron & Steel	Hamilton, Toronto	Ontario
131097	1843	Open Burning - Scrap Tires	Columbus	Ohio
132093	1349	Iron & Steel and Petroleum Refining	Chicago	Illinois and Indiana
128093	1323	Primary Nonferrous Metals		Indiana and Kentucky
129090	1140	Petroleum Refining		Illinois and Missouri

5.1 IADN and NAPS monitoring stations

IADN station information is obtained from their website: http://www.msc.ec.gc.ca/iadn [7]. NAPS data were provided by ETC of Environment Canada [8]. Most of the IADN's stations are located in rural and undeveloped areas with data representative of the background ambient air for each of the five Great Lakes. NAPS has stations all over Ontario and other major cities in Canada that monitors ambient air BaP concentration in both urban and rural areas, refer to Figure 1. The analytical methods from both programs have some variations [9].

5.2 Ambient BaP concentrations in 2003

Both IADN and NAPS measure BaP in both particle and gas phases. However, almost all BaP is present in the particle phase at ambient temperature [10]. 2003 annual average BaP concentrations from IADN and NAPS are provided in Figures 4 and 5. These are the average of numerous data points measured in an interval of every 12 days in 2003. As can be seen, local BaP releases correspond well to the ambient air BaP concentrations. This applies to almost all the monitoring stations of NAPS and IADN.

The existing monitoring data show that the highest BaP concentrations are identified in three regions-Chicago (498 pg/m^3), Hamilton/Toronto (100–300 pg/m^3), and Windsor/Detroit (380 pg/m^3). Comparing the local BaP releases indicate that high BaP releases in both Chicago and Hamilton/Toronto areas are a significant factor leading to high ambient BaP concentration. The map also shows that low ambient concentrations of BaP might be a result of the low local BaP releases. The only exception is with the Windsor/Detroit site, where a higher ambient air BaP (380 pg/m^3) is detected with a low annual release. This points to a need to further investigate both the air monitoring data and the BaP inventory. It is possible that some sources of BaP in Windsor/Detroit area were not well documented in the inventory.

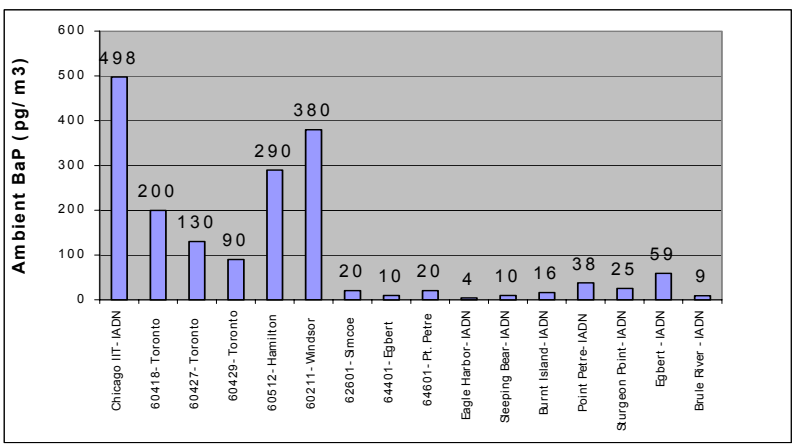

Figure 5: 2003 annual average BaP concentrations.

5.3 Trending of IADN data

The trending of IADN's BaP ambient air concentrations from 1990–2004 on six rural stations is plotted in Figure 6. These stations are located in Eagle Harbor for L. Superior, Sleeping Bear for L. Michigan, Burnt Island for L. Huron, Point Petre for L. Ontario, and Sturgeon Point for L. Erie. As shown, annual average air concentrations fluctuated with years since 1990. It does not show a clear decreasing trend. These sites are located in rural or undeveloped areas with low

local BaP releases that are well below 100 kg/y in each grid cell, refer to Figure 4 for details. The ambient BaP concentrations are slightly higher on the sites for L. Ontario and Lake Erie, which might be the result of a higher BaP release in the area.

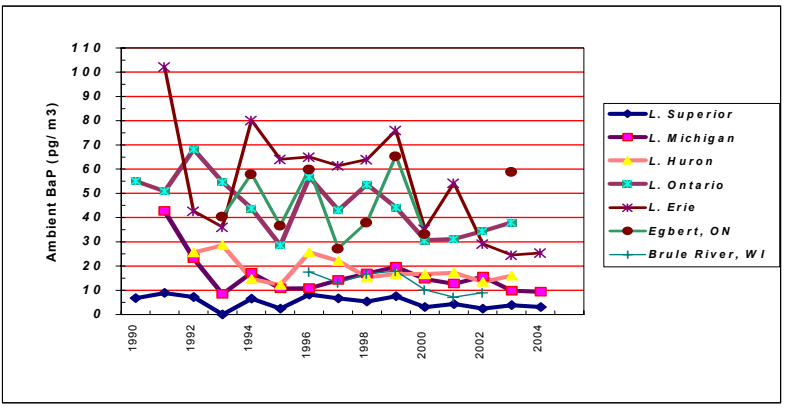

Figure 6: Trend of ambient BaP concentrations in the Great Lakes from IADN.

The BaP release data for multiple years for the grid cells in which these sites located are not available, so it is difficult to prorate the impact the local or non-local release has on the ambient air in these areas. It is likely that the releases in these grid cells have been very low in the past 15 years that a slight or no change in annual release did not bring a significant impact on the ambient air BaP concentration. This might explain why there is no clear decreasing trend on the monitoring data for these sites. It is not well known what size of the grid cell or spatial coverage is a good representation of a local release. However, the size of 1° latitude x 1° longitude (100 km x 100 km) is used in this paper.

5.4 Trending of NAPS data

The NAPS's monitoring stations are located in cities and some rural areas, refer to Figure 7 for details. As aforementioned, BaP air pollution is a local release issue and it is believed that the monitoring sites that are located in a grid cell representative of the local release are better indicators of the local BaP release trending. There are four monitoring stations located in the grid cells with higher BaP releases, so these sites are used to track the trending of ambient BaP from 1995–2003. These stations are: 60418-Toronto, 60512-Hamilton, 60211-Windsor from NAPS and Chicago IIT from IADN. The monitoring data are plotted in Figures 7 and 8. As shown, the ambient BaP on 12 rural and urban sites from NAPS and IADN does not show a clear trending from 95-03, which might be the result of the fluctuation of annual BaP releases in the vicinity of these sites. There is no obvious declining trend of BaP in Toronto, Windsor, Chicago, and almost all the other stations. This might be the result of no

significant reduction of local BaP releases on these stations. An exception is with the Hamilton monitoring site. The station is located in the grid cell that is representative of the local BaP release. Its monitoring data show a declining trend of BaP in the ambient air in eight consecutive years from 1996–2003. It agrees very well with the declining trend of local BaP releases due to the significant reduction of BaP from major source sectors in that area.

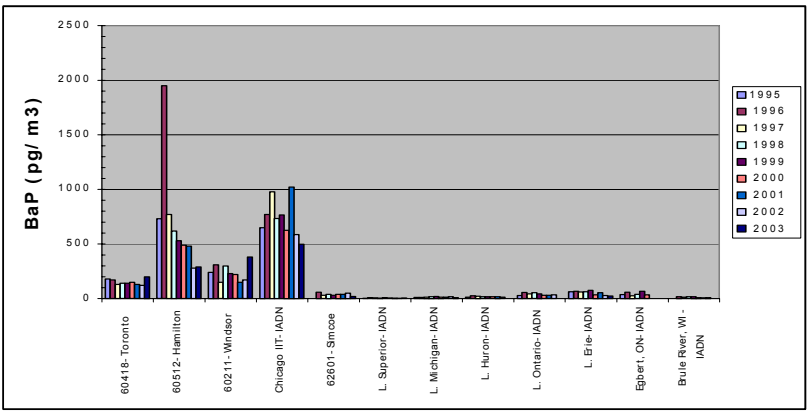

Figure 7: Annual variation of ambient BaP concentrations at major stations.

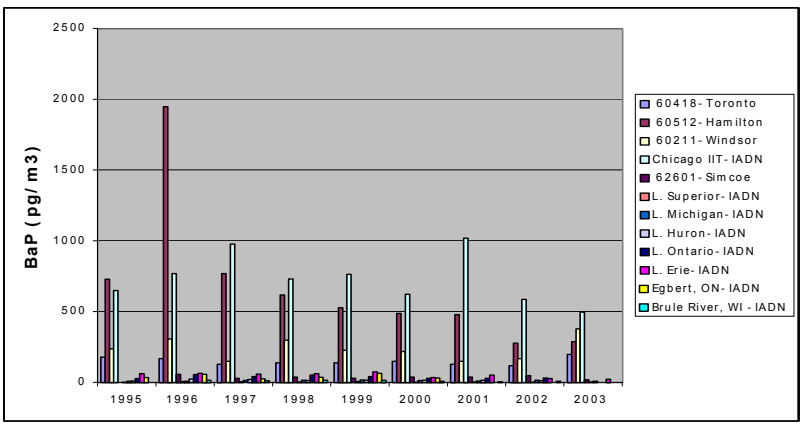

Figure 8: Annual average BaP concentrations 1995–2003.

6 Conclusions and recommendations

There are about 27,000 kg (59,400 lbs) of BaP released in 2003 in the Great Lakes Basin, of which 70% was from the U.S. and 30% from Canada. A gridded release inventory is used in this paper to locate the BaP in each county/municipality of the Basin. The size of the grid cell can be chosen so that

it is representative of the local BaP release for the areas of interest. The common major source sectors in both U.S. and Canada are residential wood combustion, steel manufacturing, primary metals production, scrap tire burning, household waste burning, and motor vehicles.

There are five grid cells in the Basin having highest BaP releases – each contributes to 4–5% of the Basin total. They are located in Illinois, Columbus, Indiana, and Ontario. It is believed that the source sectors in these areas such as iron & steel industry, scrap tire burning, petroleum refining, and primary non-ferrous metals production contributed significantly to the higher ambient BaP concentrations. This paper points to some directions on the possible data gaps on estimating BaP releases from non-point and mobile sources for both Canadian and U.S. inventories.

Local source contributes significantly to the elevated ambient air BaP concentrations. This explains why ambient BaP in urban is much higher than rural areas. The monitoring sites that are located in a grid cell representative of the local release are better indicators of the local BaP release and reduction trending. Therefore, monitoring sites should be properly selected to better indicate the local BaP reduction. There is no evidence of decreasing trend in most of the monitoring stations, such as in Toronto, Windsor, or Chicago. The reasons could be that there is no significant change of the local release regardless its release was high or low from the beginning. An exception is with Hamilton monitoring site. The station is located in the grid cell that is believed to be representative of the local BaP release. Its monitoring data show a declining trend of BaP in the ambient air in eight consecutive years from 1996–2003. It agrees very well with the declining trend of local BaP release due to the significant reduction of BaP from major source sectors in that area.

The monitoring data for the past 10–15 years show higher ambient air BaP are located in the areas with higher BaP releases. This is true for almost all the monitoring sites of IADN and NAPS with an exception with the Windsor/Detroit site, where a higher ambient air BaP (380 pg/m^3) is detected with a low annual release in less than 500 kg/y. This points to a need to further investigate both the air monitoring data and the BaP inventory. It is possible that some sources of BaP in Windsor/Detroit area were not well documented in the inventory.

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Traffic pollutant emissions in Barreiro city

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Abstract

Urban traffic is becoming a major problem, since most people use their own private car for all kind of trips, increasing the traffic congestion and atmospheric pollution. The purpose of this work was to study the atmospheric pollutants dispersion in Barreiro highway (IC21), in two specific situations, a traffic lights crossroad and a roundabout. The pollutants studied were traffic related pollutants, such as nitrogen oxides (NO_x), particulate matter (PM) and CO (carbon monoxide). A traffic counting field campaign and particulate matter measurements were carried out in the light traffic crossroad and in the roundabout of the highway. Data from monitoring network stations was also collected. All this information was introduced in a dispersion model (ADMS-urban), to obtain a spatial simulation of the pollutants dispersion. Vehicle number, class and speed, fuel type, time of the day and urban street canyon were the traffic related parameters used by the model. Meteorological variables, such as wind speed and direction, relative humidity, temperature and heat flux were also taken into consideration to understand pollutant behaviour. The model results show the pollutants dispersion, on the IC21 highway, in two different meteorological scenarios: winter and summer. Winter seems to be the worst scenario for NO_x and CO background concentrations, whereas PM tends to deposit due to rain, decreasing its concentration in this season. In summer, ozone (O_3) concentration increases due to the photochemical reaction with some pollutants such as NO_x. Analysing PM emissions, in the specific situations of light traffic crossroad and roundabout, on the IC21 highway, environmental advantages were found in the roundabout, despite its larger traffic flow, as it has a smaller PM concentration, even though it is above the legal limits.
Keywords: urban traffic, atmospheric pollutants, urban environment.

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1 Introduction

In modern society, transports have a vital role in national and international economy. However it is important to promote sustainability policies, to guarantee the balance between the economy and the environment.

Nowadays, air pollution from road vehicles is one of the most serious problems in urban areas management. The pollutant species most often of concern from road traffic sources are carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM) and ozone (O_3).

Traffic pollution has negative impacts on health and welfare, damaging builds and natural environment. According to World Health Organization (WHO), mortality and morbidity have increase due to road traffic-related air pollution. Several studies show that sensitive groups, such as children, elder and people with chronic problems are likely to be affected to air pollution at lower levels then the general public.

The aim of this work was to study the impact of traffic in atmospheric pollution dispersion in Barreiro highway (IC21), with special attention for two specific situations, a traffic lights crossroad and a roundabout.

According to several authors, roundabouts have more advantages to control intersection traffic than crossroads: reducing the waiting times, decreasing the road speed and consequently the reduction of car accidents and atmospheric pollution.

The dispersion of traffic air pollutants is determined by many factors, such as meteorological conditions (wind speed and direction, temperature and humidity), atmospheric turbulence, occurrence of inversion layers, mixing height (Karppinen [1]) and urban topography, that can trap and limit pollutants dispersion, due to lack of wind flow out of the canyon (street canyon), (Park [3]).

2 Method

2.1 Location

Barreiro is a Portuguese city with approximately 80,000 inhabitants distributed over 34km^2. The city is located about 40km south of Lisbon on Tagus River south margin (Figure 1). It's an almost flat region, with the highest point at approximately 10m above sea level.

2.2 Field campaign

2.2.1 Traffic field campaign

To study road traffic pollutant emissions, a field campaign was carried out in the main streets of Barreiro city. In this campaign, vehicle counting was made according to the vehicle class - light-duty vehicles (LDV), heavy-duty diesel vehicles (HDDV), buses (Bus) and motorcycles (MC). The campaign took place during 5 days (Spring 2005), in the rush hour (8:00-9:00am; 9:00-10:00am; 5:00-6:00pm and 6:00-7:00pm) for most congested streets and out of the rush hour for

others, where traffic is approximately constant all over the day. In this work, a crossroad and roundabout, in IC21 highway, were the specific cases chosen to understand the influence of the traffic control devices on traffic and on pollutants emission. Counting was made during one hour in each case.

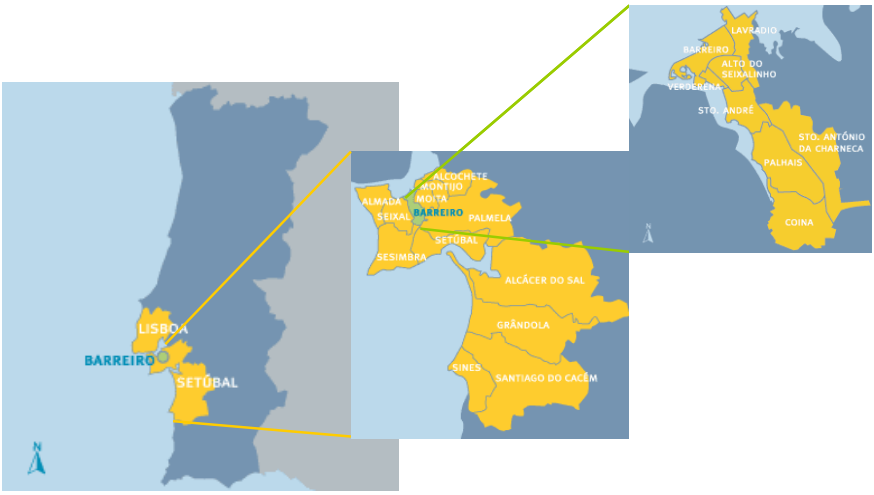

Figure 1: Barreiro city location (source: Barreiro council).

Figure 2: Crossroad and roundabout of street IC21.

IC21 is asphalted, with two-ways, measuring 26m and with some buildings along the road.

2.2.2 PM_{10} and meteorological variables monitoring field campaign

Simultaneously with the traffic counting, PM with less than 10μm diameter (PM_{10}) was hourly measured by a Beta Gauge Dust Monitor. These measurements allowed quantifying PM10 concentration levels in each case and compare them. Meteorological conditions were also registered, namely temperature, humidity and wind speed and direction.

Table 1: Shows the results of vehicle counting in each point, as well as the measured PM_{10} concentrations. Some counting points have more than one value, corresponding to cross streets.

Case	*Counting Points*	*LDV*	*Bus*	*HDDV*	*MC*	*PM_{10} measurement ($\mu g/m^3$)*
IC 21 crossroad	1	469	3	42	3	137,0
	2	403	0	3	6	
	3	36	1	2	0	
	4	523	5	0	3	
	5	192	1	2	1	
	6	92	0	0	6	
	7	301	1	4	2	
	8	549	0	7	4	
	9	179	10	8	3	
	10	610	2	54	0	
	11	36	3	6	0	
	12	192	9	2	1	
IC 21 Roundabout	1	412	4	56	2	68,5
	2	608	18	10	10	
	3	320	2	8	14	
	4	820	18	62	10	
	5	1020	12	44	4	
	6	148	0	2	4	
	7	652	22	16	6	
	8	524	6	50	8	

The black spot represented in Figure 2 is the PM measurement equipment.

2.3 Simulation work

2.3.1 Road sources

The results from the field campaign, vehicles parameters and street characteristics were introduced in simulation models. Firstly, in MOBILE 6.2 (EPA [5]), a software used to calculate emissions factors, were introduced vehicle and meteorological parameters, obtaining CO, NO_x, and PM vehicle emission factors. Emission factors are average emission rate of a given pollutant for a given source, relative to units of activity. These emission factors and urban street canyon characteristics were introduced in ADMS-Urban 2.0 (CERC [6]) to calculate pollutants dispersion; however other parameters that will be tackled bellow are also essential to this model.

2.3.2 Grid sources

Grid sources are defined as residual, poorly-defined or diffuse emissions in urban areas, like domestic heating and secondary roads (CERC [6]). Due to the pleasant weather in Barreiro city, only secondary roads were considered. The characterization of this source was made according to the resident population and

the number of vehicles in Barreiro city (Eurostat [7]) and considering only one vehicle class (LDV). These data were also introduced in MOBILE 6.2 and the results in ADMS-Urban in an identical way of road sources. The results were aggregated as a grid source in ArcView 3.1 to achieve the results of diffuse emissions.

2.3.3 Background data

Pollutants transported from other regions and produced by nature, that is to say not generated by local sources, are considered to be the background pollution, and are hourly measured by background air quality monitoring stations managed by Coordination and Regional Development Commission of Lisbon and Vale do Tejo (CCDR-LVT). SO_2, NO, NO_2, NO_x, PM_{10}, CO and O_3 (Ozone) are the pollutants measured by these stations. These data was also introduced in ADMS-Urban 2.0.

2.3.4 Meteorological data

Meteorological data have an important influence in pollutants behaviour. The meteorological data were supplied by the Portuguese Meteorological Institute, from a climatic acquisition station located in Lavradio (Barreiro). The use of a climatic study of 30 years, made by Meteorological Institute from Portugal, allows the understanding of pollutants behaviour, for the most frequent meteorological conditions, which occurred in the region for a long period of time. The most important meteorological variables used were wind speed and direction, temperature, humidity and heat flux (calculated by the model), which allows one to distinguish the most frequent conditions for winter and summer time.

Atmospheric stability is other very important parameter. In this study, the most frequent atmospheric stability for this region, neutral, was considered (Domingos et al [8]). Meteorological data was introduced in ADMS-Urban 2.0, which uses FLOWSTAR 7.0 also from CERC (CERC [9]), to treat all meteorological and topographical information (characterize below).

2.3.5 Topography and roughness data

Topography and roughness have a great influence on the atmospheric flow, and consequently on the pollutants dispersion. Topography data were supplied by the Geographical Army Institute of Portugal (IGEOE) in VPF format, and converted to ASCII format. The roughness matrix was developed using Corine Land Cover maps supplied by the National Geographical Information Centre (CNIG). These data are also treated in FLOWSTAR 7.0 model from CERC and introduced in ADMS-Urban, as it was already referred.

Figure 3 presents a schematic representation of all the simulation work done.

3 Results and discussion

Mobile 6.2 calculates emission factors for all mentioned pollutants, but the treatment for PM is different, since this pollutant results from the combustion

process, like other pollutants, but also from brakes lining, tyres, car body, re-suspension of road and soil dust (Marko [10]). The model has calculated PM from exhaust pipe, brakes and tyres, emitted by Light Duty Gasoline Vehicles (LDGV), Light Duty Diesel Vehicles (LDDV), MC, HDDV and Bus (Coelho [11]) (Figure 5) and also CO, NO_x and PM contribution from combustion process (Figure 4). Analysing the results, high CO contribution was found in LDGV (almost 100%), NO_x had a smaller contribution, however also in LDGV (40%) and HDDV (30%), whereas PM main contribution was in LDDV (60%). The low concentrations of CO in diesel vehicles are counterbalance by the high concentration of NO_x, due to higher combustion temperature.

Concerning the different sources of PM, it can be noticed that the PM10 emission factor from exhaust pipes is highest for diesel vehicles, while brakes and tires are the most important sources for gasoline vehicles.

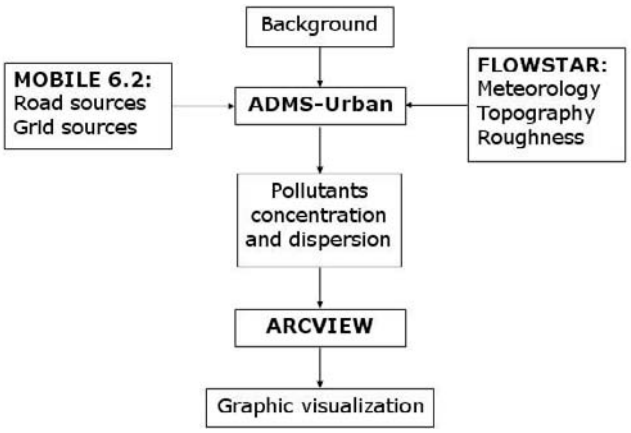

Figure 3: Schematic representation of simulation work.

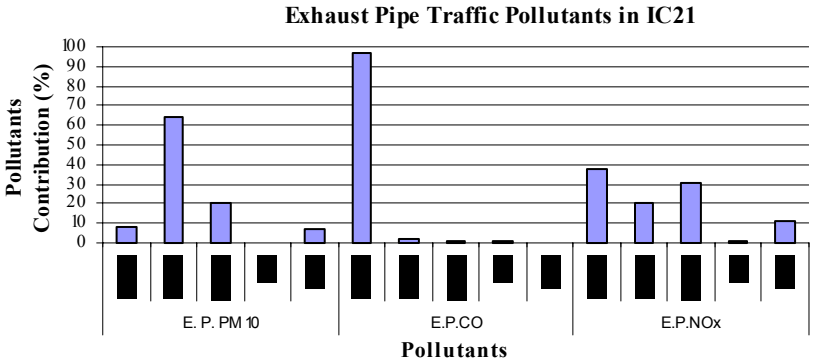

Figure 4: Exhaust pipes pollutants contribution in IC21.

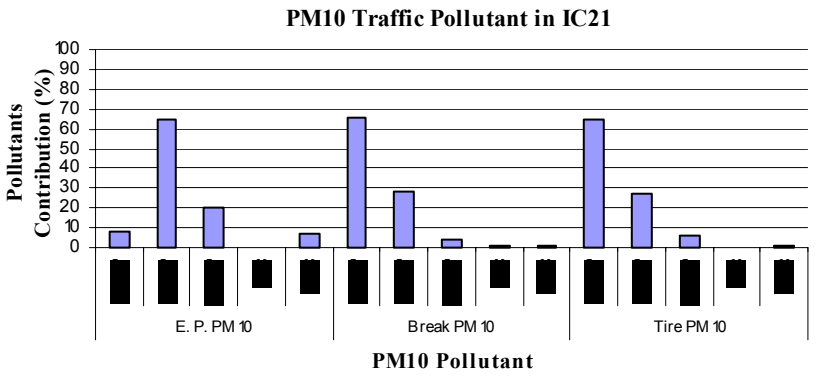

Figure 5: PM_{10} contribution in IC21.

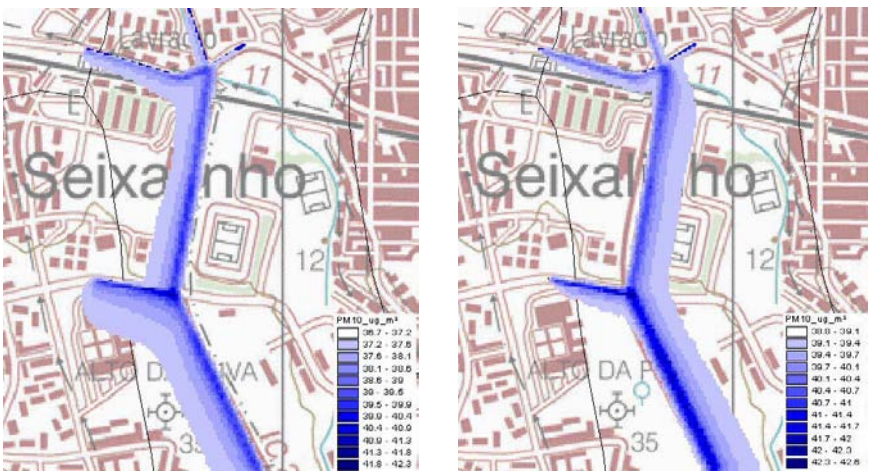

Figure 6: PM_{10} dispersion and concentration in winter (left) and summer (right).

The sum of the emission factors from all PM sources was used to quantify PM emitted by the vehicle:

$$PM_{10} = Exhaust\ pipe + Brake + Tyre \quad (1)$$

PM_{10} represents the total emission factor (g/km), while exhaust pipe, brake and tyre denote the contributions of the different sources to the total emission factor. This value was used in ADMS-Urban dispersion model taking into consideration the number of vehicles counted.

Pollutants behaviour, for most frequent meteorological conditions in winter and in summer time, was simulated by ADMS-Urban. The results for the studied road (IC21 highway, are graphically represented in Figure 6 (PM_{10}), Figure 7 (CO) and Figure 8 (NO_x)

Figure 7: CO dispersion and concentration in winter (left) and summer (right).

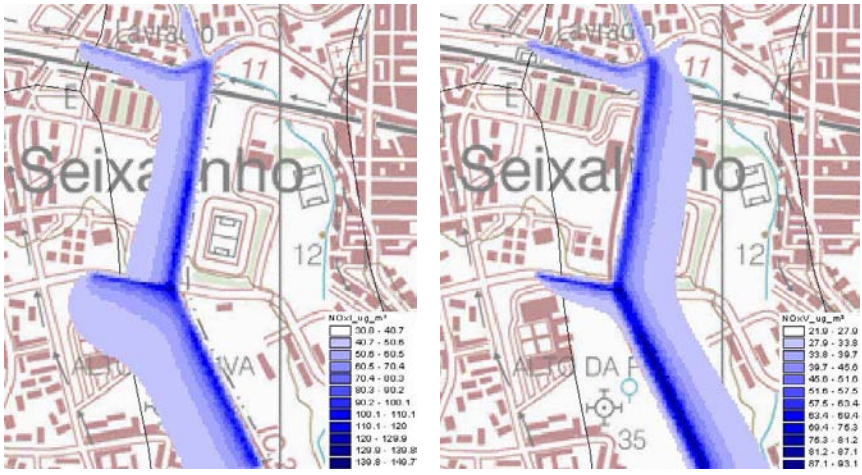

Figure 8: NO_x dispersion and concentration in winter (left) and summer (right).

According with simulations none of the pollutants exceed the legal limits. CO and NO_x present higher levels in winter, whereas PM_{10} presents in summer. The high PM_{10} concentrations measured in IC21 (Table 1) are justified by the measurement period, the rush hour, the nearness of vehicle emissions outlet and meteorological conditions, since the low wind speed doesn't allow a good dispersion.

Despite both intersections high PM_{10} concentration, traffic light crossroad had a higher level of particles, due to the waiting and stops and due the road slope, which demands more intense acceleration.

4 Conclusions

Air pollution due to transports is a real problem, being essential to promote a sustainable development, to balance the economy and the environment. Traffic pollution is more easily breathed, since is emitted near the surface, where people walk, almost without any dispersion.

Urban traffic management must be very seriously contemplated in Urban Management Plan, choosing the best infrastructures to control traffic, which, according with some studies, the roundabouts are included. In this study the PM_{10} measurement can support this idea, since higher concentrations were found for the traffic light crossroad.

In what concerns to vehicle type, LDGV show to have a larger contribution to CO and NO_x emissions. In PM_{10} emissions, sources were divided, being LDGV the main cause of PM_{10} from breaks and tyres and LDDV the cause of PM_{10} exhaust pipe.

The high levels of PM_{10} measurements, must take into account the specific conditions of low wind, the nearness of measurement equipment from the source and the fact that the measurement was made in a rush hour.

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Source apportionment of VOC in 3 French sites by CMB and PMF models and critical analysis

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Abstract

Hourly concentrations of 31 ambient volatile organic compounds (VOC) were analysed between 2001 and 2003 at three sites located close to three large French cities, in order to calculate contributions of each VOC source. Winter and summer VOC datasets were analysed using chemical mass balance (CMB) and positive matrix factorisation (PMF). For each site, some common sources (vehicle exhaust, gasoline evaporation, leaks of gas, biogenic and domestic heating) were found. Whatever the site of measurement, the automobile exhaust source is most important (35.4 to 61.4% of the total contributions according to the season and the site) in terms of contribution of source. First PMF and CMB results are quite different because PMF finds factor relating to distant sources. New CMB modelling using distant sources profile were made and so CMB and PMF exhibit nearly identical solutions.
Keywords: volatile organic compound, urban-periurban-rural sites, data analysis, source apportionment, receptor modelling.

1 Introduction

The volatile organic compounds (VOC) are important trace species emitted into the atmosphere from anthropogenic and biogenic sources [1], which can influence its chemistry in many ways [2].

In France, VOC measurements are carried out by air quality monitoring networks. Continuous hourly measurements of 31 VOC from C2 to C9 have been performed since 2001 in three regional networks (Marseille, Strasbourg and Grenoble) and so a big VOC concentration database is now available. Each site presents a specific typology: urban site for Marseille, periurban site for

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Strasbourg and rural site under industrial influence for Grenoble. The sources likely to influence the ambient concentrations of VOC on each site were systematically indexed and three databases were made up starting from the VOC concentrations data.

In recent years, many studies have been conducted on VOC ambient [3–7]. In the same way, many studies explain CMB [8–10] or PMF [11, 12] results on VOC datasets. However, among these studies a restricted number relates to a comparison between PMF and CMB results [3, 13]. According to our exceptional dataset (more than 1.200.000 data), source apportionment was performed and receptor models were applied to VOC data divided into seasonal periods (summer and winter).

So, in the present study, the objectives are:

- to use receptor models to calculate relative contributions of each source at the three sites
- to compare PMF and CMB results
- to optimise CMB modelling according to PMF results

2 Field studies and sampling sites

We systematically listed the whole of the VOC sources likely to influence the three receptor sites located near 3 large French cities. This localization is necessary. Indeed, without a good knowledge of the sources likely to influence the ambient concentrations, it will be impossible to insert good profiles sources in the CMB and to explain the results of the different modelling especially for PMF modelling.

2.1 Marseille Site (43°16' N, 5°23' E)

For this site, the VOC measurement is led at the Prado station which also corresponds to the central station of Marseille air quality monitoring network (AIRMARAIX) located in the southern half of the city on one of the busiest arteries (27,000 vehicles/day) of Marseille. It is an urban station. In a radius of 1 km around the measurement site, there are seven laundries, four little printing works or painting companies and more than twenty garages or petrol stations. In addition to the specific sources of emission which have just been located, the sources of emission likely to influence the site measurement are the automobile traffic of the Prado Avenue, the adjacent streets and one partly underground highway (A50). Lastly, a chemical factory specialized in the manufacture of an amino acid (approximately 10 km in the east of the site, 358 $t.y^{-1}$ of VOC) has been located.

2.2 Strasbourg Site (48°36' N, 7°42' E)

For Strasbourg, the VOC measurement is led on the Strasbourg central station of air quality monitoring network (ASPA). This sampling site is in Schiltigheim, town of approximately 31,000 inhabitants situated next to Strasbourg. It is a periurban site. The presence in the vicinity (approximately 50 m) of the receptor

site of a small gasoline depot is able to influence VOC concentrations. Taking into account the localization of the site, only a few local sources can be at the origin of ambient VOC concentrations. Consequently, some industrial sites relatively strong VOC emitters (refinery, production of elastomers, printing works) but quite far away from the receptor site (more than 2 kilometers) are able to influence the measured concentrations.

2.3 Grenoble Site (45°06' N, 5°43' E)

For the zone covered by the Grenoble network (ASCOPARG), the VOC measurement is led on a rural station under industrial influence: the Champagnier station. The sampling site can be described as slightly influenced. Indeed, it does not have activities recognized like strongly emitting of VOC (laundry, garage, petrol station,) except the relatively limited automobile traffic (proximity of a secondary road). Consequently, the station could mainly be subjected to the action of a near factory site which mainly produces polychloroprene rubber. The site could also be influenced by the emissions of more distant industries such as the chemical pole of Jarrie (production of synthetic gems and basic chemicals) or the emissions of Pont de Claix industries (manufacture of chlorinated compounds, inks production and printing works).

3 Receptor models

For this study, we have used the Chemical Mass Balance (CMB) [14–16] and Positive Matrix Factorization (PMF) [17, 18].

CMB predicts the contribution of different sources to measured receptor concentrations using an inverse variance weighted least-squares linear regression. Mathematically the system is written:

$$C_{ik} = \sum_{j=1}^{p} F_{ij} \cdot S_{jk} \qquad i = 1,...,m\,;\; k = 1,...,n \tag{1}$$

where C_{ik} is the concentration of compound i for the k observation, F_{ij} is mass fraction of compound i from source j (weighting percentage), S_{jk} is the contribution of source j for the k observation (μg/m^3).

In contrast to other receptor models (PMF and UNMIX for example), which extract source compositions from the data, CMB requires the user supply source profiles. Also in contrast to the other models, CMB is applied separately to each observation, rather than operating on the data set as a whole. Assumptions made in using CMB and more details on mathematical resolutions have been discussed elsewhere [14]. CMB is largely used for environmental data and generally produce good results for VOC data [13, 19].

PMF is a multivariate receptor model, which analyze a data series of n observations simultaneously in an attempt to determine the number of sources, p; their chemical composition, F_{ij} ; their contributions to each observation S_{jk} and the residual error, ε_{ik} such that:

$$C_{ik} = \sum_{j=1}^{p} F_{ij} \cdot S_{jk} + \varepsilon_{ik} \qquad i = 1,...,m\,;\; k = 1,...,n \tag{2}$$

The resolution of the equation is done by minimization of Q.

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{\varepsilon_{ij}}{\sigma_{ij}} \right)^2 \tag{3}$$

where σ_{ik} is the variation of the data point.

In PMF, the user chooses the number of factors p. Two parameters can help to choose between different sources numbers in order to obtain the optimal number of sources :

❶ IM : "the maximum individual column mean"

❷ IS : "the maximum individual column standard deviation"

More details are given by Lee et al. [20].

4 Results

For this study, the dataset of each site has been divided into summer (June–August) and winter (December–February) periods.

4.1 CMB results

For CMB modelling, the whole of the profiles relating to the VOC sources highlighted during the sources indexing (see section 2) were tested. First modelling will be done with the whole of the sources profiles likely to influence the concentrations on the receptor sites. Then, this modelling is repeated by removing the profiles of the sources giving negative contributions or standards errors larger than the contribution value [8]. Indeed, although present on the study area, some sources cannot contribute significantly to the ambient concentrations. For the sources which influence the receptor site, denominations are given in table 1. Whatever the season and the site, very few sources seem able to influence ambient concentrations (table 2). There are 5 common sources (vehicle exhaust, gasoline evaporation, leaks of gas, biogenic and domestic heating) to which we must add:

- rubber factory source for Grenoble
- printing works and solvent sources for Strasbourg
- printing works, solvent use and amino-acid factory sources for Marseille

Whatever the site of measurement, the automobile exhaust source contribution is most important (35.4 to 61.4% of the total contributions according to the season and the site). Despite the fact that Marseille is the most urban site, the share of the vehicle exhaust source is the weakest of the three sites. Consequently, relative percentage of vehicle exhaust source depends not only on urban traffic intensity but also on the number and the intensity of the other sources and we must be careful not to give hasty conclusions.

Table 1: Summary of the sources influencing the three receptor sites.

Name	Description
EXHAUST	Traffic exhaust
EVAP	Gasoline evaporation
LEAK	Leak of gas
BIOGENIQUE	Biogenic sources
HEATING	Domestic heating
SOLVENT	Solvent use
PRINTING	Printing works
RUBBER	Rubber factory
AA FACTORY	Amino acid factory

Table 2: Relative contribution of the different sources on the three receptor sites according to the season.

Source	Marseille		Strasbourg		Grenoble	
	summer (%)	winter (%)	summer (%)	winter (%)	summer (%)	winter (%)
EXHAUST	35.4	41.1	46.0	53.8	58.9	61.4
EVAP	25.6	21.3	22.2	18.6	16.4	9.5
LEAK	9.2	14.6	16.6	18.7	15.9	17.4
BIOGENIQUE	0.7	-	0.8	-	2.4	-
HEATING	-	0.3	-	3.3	-	9.5
SOLVENT	20.0	9.3	13.1	5.2	-	-
PRINTING	2.1	3.8	1.4	0.5	-	-
RUBBER	-	-	-	-	6.4	2.1
AA FACTORY	6.9	9.6	-	-	-	-

On each sampling site, the gasoline evaporation source is overall the second more important source. Thus, the automobile traffic through the evaporation and exhaust sources is very mainly responsible for the measured VOC concentrations (between 61 and 75.3% of the total contents). This result is in agreement with other CMB results obtained elsewhere [9, 21]. In addition, the contribution of gasoline evaporation source is stronger in summer when the higher temperature allows a stronger hydrocarbons evaporation. In agreement with the urban location, the lowest latitude and the increased sunlight of the Marseille site, the contribution of the source gasoline evaporation is the strongest compared to the other sites. Besides, the clear difference between the percentages of this same contribution for the site of Strasbourg (22.2% the summer and 18.6% the winter) and Grenoble (16.4% the summer and 9.5% the winter) can be explained by the presence of a fuel depot near the Strasbourg site.

For the three receptor sites, the leak of gas source is one of the major sources. However, bibliography shows that the share of this source, in the case of urban studies, is not negligible [9, 22, 23]. Taking into account the life times of the two major compounds of the profile of this source (τ(ethane) = 23 days and τ(propane) = 5 days), it is sometimes difficult to distinguish the share taken by

the contribution of old air masses brought back by air transport towards the sampling site. Thus, Hellén et al. [10, 24] integrates the concept of "remote sources" in her work with a profile mainly associated with alkanes (20 to 24% in mass for ethane and 15 to 18% for propane depending on the season).

Biogenic source appears only during the summer period when sunlight and temperature are higher [25]. The results show particularly an important percentage (2.4%) for this source for Grenoble site mainly due to forests in the vicinity.

Generally domestic heating source misses for studies using CMB. In our case, among the four profiles tested, only the profile resulting from GENEMIS database could give satisfactory results. Considering the exclusively winter character of this source, the contribution of the source "domestic heating" is quantifiable only during this season. On Grenoble site, taking into account the lower urban density (limitation of the number of sources influencing the site) and the average winter temperature very low (between 0 and 2°C), the domestic heating source has one of the strongest contributions.

Solvent use source could be quantified only on Marseille and Strasbourg sites. Indeed, the site of Grenoble is distant from any activity being able to use solvents.

The three other sources which were listed are of industrial origins. Their contributions can present an important percentage (up to 9.6%) and a seasonal variation.

4.2 PMF results and discussion

PMF modelling were made initially on the Grenoble data. The optimal numbers of sources p were chosen according to the two parameters described in section 3. Best results were obtained with 7 factors for winter and summer dataset. In order to compare PMF and CMB results, factors modelling exhaust due to diesel and gasoline were combined in one profile (figure 1).

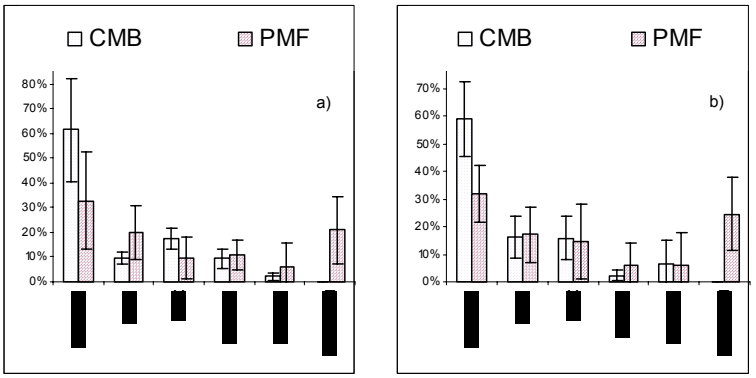

Figure 1: Comparison between CMB and PMF results for Grenoble data. a) winter period. b) summer period.

The results of figure 1 show a clear difference (about 30%) for the percentage of the exhaust source contribution calculated by the 2 models. For the other sources, contributions are similar taking into account uncertainties (standard deviation of calculated contribution). However it seems, for winter modelling, that the PMF over-estimates the contribution of the gasoline evaporation source (same contribution winter and summer) and under-estimates the contribution of the leak of gas source. In addition, an unknown source (about 20% of total contribution) was found by PMF for summer and winter dataset.

To complete this work, we have tried to identify the unknown source. The latter is principally composed of alkanes (ethane 34.1%; butane 15.5%). In recent articles, Héllen et al. [24] and Gouw et al. [26] describe distant sources emissions which during their transport are oxidised remaining thus the less reactive species such as alkanes. Consequently, our unknown source could be a distant source. Starting from the Grenoble dataset, we tried to find observations made in high wind conditions, at night and preferably at week ends. Thus, the influence of the local sources (especially traffic exhaust) will be minimized, and we will be able to reach an approximation of the concentrations profile due to the distant sources (extreme conditions VOC profile). Figure 2 shows the comparison between PMF unknown factor and extreme conditions VOC profile for Grenoble summer data. The two profiles are nearly identical and it seems that PMF was able to distinguish the distant sources in the ambient concentrations.

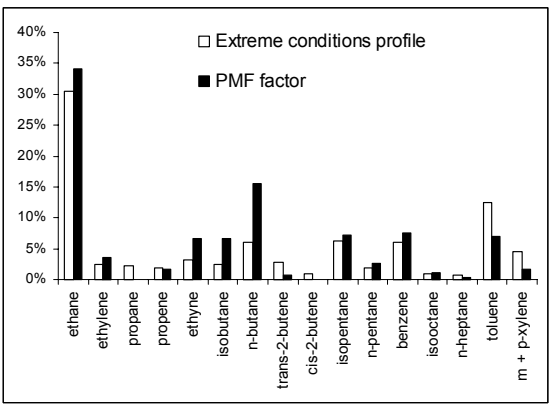

Figure 2: Comparison between PMF unknown factor and extreme conditions VOC profile for Grenoble site and summer data.

4.3 New CMB modelling

Considering the previously results, we made new CMB modelling on Grenoble summer dataset with the profile (created above) corresponding to distant sources. Thus, the whole of the sources influencing the site of Grenoble the summer will be (this time) entered in CMB model. The results show an average contribution of about 40% for exhaust sources and 20% for distant sources. For the other

sources relative contributions are globally unchanged. Finally, CMB and PMF exhibit, now, nearly identical solutions. Thus, CMB users finding strong contribution for the exhaust source (without using profiles relating to the remote sources) must pay attention. Indeed exhaust source contribution can be over-estimated. Future tests on the Strasbourg and Marseille data will be carried out in order to know the global influence of the distant sources.

5 Conclusions

Hourly concentrations data of 31 VOC measured on three sites located close to three large French cities were analysed using chemical mass balance (CMB) and positive matrix factorisation (PMF). For each site, five common sources (vehicle exhaust, gasoline evaporation, leaks of gas, biogenic and domestic heating) were found. Whatever the site, the automobile exhaust source is most important (35.4 to 61.4% of the total contributions according to the season and the site) in terms of contribution of source. An increase of evaporative source contribution (gasoline evaporation and solvent use) was observed during the passage from the winter months to the summer ones. Two sources appear only during one season: the biogenic source presents a quantifiable share only during the summer months when sunlight and temperature are higher and the heating source is lost during the passage from the winter months to the summer ones. The latter has a strong contribution on Grenoble site taking into account the low number of sources influencing the site and the very low average winter temperature. The industrial sources can have important percentage (up to 9.6%). First PMF and CMB results on Grenoble dataset are quite different because (i) PMF finds unknown factor which contribute to about 20% (ii) an important difference is observed for the exhaust source contribution. Study of bibliography can permit to conclude that the unknown source could be associated to a distant source. New CMB modelling on Grenoble summer dataset with the profile created with extreme conditions corresponding to distant sources was made. So CMB and PMF nearly exhibit identical solutions and CMB users studying rural site must pay attention not to over-estimate contribution of exhaust sources.

Acknowledgements

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Simulation of fuel consumption and emissions in typical traffic circumstances in Belgium

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Abstract

During the execution of the project Floating Automotive Data Collection (FADC), various traffic conditions were recorded using in-vehicle measurements. A series of reference measurements were performed on a fixed route in Belgium in real traffic circumstances, including motorway, rural and city traffic. Three vehicles were used for the reference measurements: a passenger car, a delivery van, and a delivery truck. An on-board device recorded vehicle speed and GPS position on second-basis. The resulting speed profiles were used as input in the vehicle emission simulation programme VeTESS to estimate fuel consumption and emissions of certain vehicles driving according to these speed profiles. The goal of these calculations was to quantify the effect of preventing traffic jams. From the simulations it was concluded that a reduction in average speed does not necessarily lead to higher fuel consumption. Actually when average speed is reduced from speeds above 100 km/h down to 80 or 60 km/h, fuel consumption can even be expected to decrease. Of course traffic jams are more about low average speeds. The simulations showed that when average speed drops below 30 or 40 km/h, fuel consumption increases significantly. Emissions of NO_x, CO and HC also increase in this case. So concerning fuel consumption and emissions it is indeed worth the effort to prevent traffic jams and slow traffic and to improve the traffic flow. The role of traffic jam detection is very important to take measures to improve the traffic flow and this way save fuel and reduce emissions.
Keywords: vehicle emissions, real traffic conditions, GPS recordings, emission simulation.

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1 Introduction

1.1 FADC project

The project Floating Automotive Data Collection (FADC) is carried out with the support of the EU-Asia Information Technology and Communications (IT&C) Programme [1]. The project involves three partners: VITO in Belgium, the University of Udine in Italy and NetPEM (Network for Preventive Environmental Management) in India [2].

The main activities in the project envisage the calibration of the fleet management functionalities of a mobile and in-built vehicle device to local requirements in India. Activities include dynamic floating data collection, quantification of fuel consumption and pollutant emissions related to traffic conditions, organization of dedicated workshops and development of a reference framework for pilot applications in specific types of roads in New Delhi, India.

1.2 Vehicle tracking and traffic jam detection

In its early stage, tracking devices were very useful to locate stolen vehicles. However functionalities can be expanded very far. Built-in functions can be added and extra sensor signals can be added to the standard registrations [2]. Especially fleet management solutions are envisaged currently. With the use of intelligent transport systems, service companies can provide live traffic data, picked up from sensors that monitor vehicle speed, combined with incident reports. The tracking device can be in direct contact with a central server or can send regular reports and data.

Within this project the idea of combining a tracking device with automated traffic jam detection was looked into.

The idea was to monitor speeds and acceleration profiles as a function of location, and automatically detect deviations from normal fluent traffic. The detection could be done on-board the vehicle and in case of traffic jam detection, the device would send a message to a central server which maps different traffic jam detection massages. The system would of course operate optimal if a sufficient number of vehicles in the traffic are equipped with such device.

2 Reference measurements

As a basis for feeding the database with typical speed profiles as a function of specific roads and road types, reference measurements were performed on a fixed route in Belgium. Comparable measurements were afterwards performed in New Delhi, India.

For the measurements in Belgium, a route between VITO (Mol) and Antwerp was defined. The route has different parts of rural, city and motorway traffic. Figure 1 shows the route and its segments on a map.

Figure 1: Test route with different road types.

11 segments were defined in the route, with typical traffic circumstances:

- Segment 1 (rural traffic around Mol): variation of average speed between 32 and 58 km/h. Variations are due to standstill at crossroads or some other traffic. No real effect of traffic jams.
- Segment 2 (city traffic in Mol): variation of average speed between 23 and 41 km/h. Variations are due to standstill at crossroads or some other traffic. No real effect of traffic jams.
- Segment 3 (rural traffic from Mol to Oud-Turnhout): variation of average speed between 35 and 54 km/h. Variations are due to standstill at crossroads, some other traffic or temporary road obstructions. No real effect of traffic jams.
- Segment 4 (motorway traffic on E34 from Oud-Turnhout to Antwerp): variation of average speed between 58 and 117 km/h. Especially the last part (11 km) from the merge of E34 with E313 in Ranst to Antwerp is sensitive for traffic jams.
- Segment 5 (motorway traffic on Antwerp Ring road): variation of average speed between 20 and 97 km/h. Ring road is very sensitive for traffic jams.
- Segment 6 (city traffic in Antwerp): variation of average speed between 8 and 26 km/h. Mind that the historic centre of Antwerp was not included, most was suburb traffic. Traffic flow here is very dependent on traffic circumstances. A lot of stand-still is recorded (between 10 and 30% of segment time).
- Segment 7 (rural traffic around Antwerp): variation of average speed between 20 and 40 km/h. This part also belongs to the surroundings of Antwerp and traffic flow also depends on the traffic circumstances.
- Segment 8 (motorway traffic on E34 from Antwerp to Geel): variation of average speed between 87 and 109 km/h. Traffic jams do not occur frequently in this part.

- Segment 9 (rural traffic around Geel): variation of average speed between 21 and 41 km/h. Very busy connection between E313 and Geel. Most standstill at crossroads and roundabouts.
- Segment 10 (city traffic in Geel): variation of average speed between 22 and 37 km/h. Variations are due to standstill at crossroads or some other traffic. No real effect of traffic jams.
- Segment 11 (rural traffic from Geel to Mol): variation of average speed between 59 and 70 km/h. Very calm traffic.

Measurements were performed with
- a passenger car (Peugeot 206 Diesel)
- a delivery van (Ford Transit)
- a delivery truck (Mercedes Atego)

Not all recorded segments have the same sensitivity to traffic jams or slow-down traffic. To visualize this, figure 2 shows all recorded average speeds on the different segments.

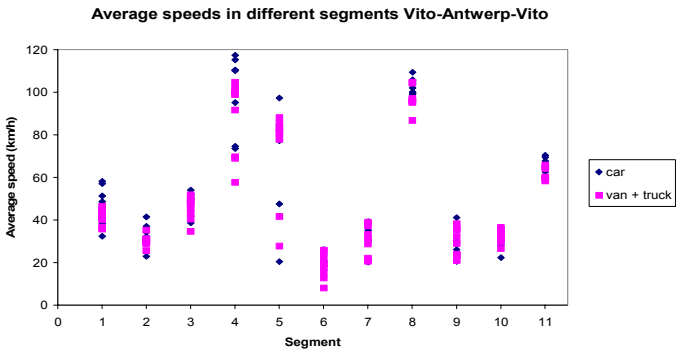

Figure 2: Average speeds recorded on the 11 segments.

3 Simulations

To quantify the effect of traffic circumstances on fuel consumption and exhaust gas emissions of vehicles, the recorded speed profiles were used as input in a vehicle emission simulation tool, called VeTESS.

3.1 VeTESS

The simulation tool VeTESS was developed within the Decade project, supported by the EC 5th Framework Programme [3]. The model can estimate fuel consumption and emissions of specific vehicles in specific journeys. The tool uses as input: the vehicle parameters, specified driver behaviour and the speed profile which the vehicle wants to achieve.

Typical speed profiles can be derived either from on-road data, either from predictions of traffic models. The emission simulation tool can then be used to estimate fuel consumption and emissions on these speed profiles.

Within the Decade project specific vehicle and engine models were made to be used in VeTESS. The following vehicle models were used for the calculations in FADC:

- VW Golf 1.9 TDi diesel passenger car (1320 kg)
- VW Polo 1.4 gasoline passenger car (1130 kg)
- Citroën Jumper 2.5D diesel delivery van (1890 kg)
- IVECO Eurocargo diesel delivery truck (7500 kg)
- MAN A12 Euro 2 diesel bus (12750 kg)
- Van Hool A600 Euro 2 diesel bus (12000 kg)

Typical vehicles weights and typical driving behaviour were assumed.

Emissions and fuel consumption of the passenger cars were simulated on the cycles driven by the Peugeot 206. For the delivery van the cycles of the Ford Transit were used. For the truck and the buses the cycles of the Mercedes Atego and the Ford Transit were used.

All cycles were divided into the 11 predefined segments.

It turned out that average speed is a very important parameter to relate fuel consumption and emissions to. In the following sections the relation of average speed with energy demand, fuel consumption and emissions of NO_x, CO, HC and PM will be highlighted.

3.2 Energy demand

Energy demand is expressed in kJ/km. It is calculated with air resistance, rolling resistance, gradients (not counted in these simulations as the route is quite flat), and acceleration. Negative values of energy demand are not counted, as no brake energy can be recuperated (as in electric vehicles).

In most cases higher average speeds have higher average energy demand. Most of it has to do with the higher air resistance at higher speeds. At lower average speeds there is much variation in energy demand, depending on standstill time, number of stops, frequent accelerations, speeds that are reached.

The buses have a much higher weight than the other vehicles, and accelerations are therefore very important in the energy demand of buses. For the buses only at very high speeds there is a significant increase of average energy demand due to air resistance.

3.3 Fuel consumption

Fuel consumption and CO_2 emissions are directly related, so only fuel consumption will be discussed here.

It would be expected that the higher the energy demand, the higher fuel consumption. This is only partly true. At higher speeds, the engine usually reaches better energy efficiency, which partly compensates the higher energy

demand. The fraction of no or low load is much higher when average speed goes down, so energy efficiency also drops.

In the figures two effects are clear:

- Below a certain speed (30 or 40 km/h) there is an increase in fuel consumption due to a lower energy efficiency at low load (or a high fraction of idling).
- Above a certain speed (100 km/h for the cars and 80 km/h for the heavier vehicles) the impact of air resistance becomes very important, leading to an increase of fuel consumption at higher speeds.

Of course all depends on the engine technology, but the two effects are clear for all vehicles. When looking at the difference between the diesel passenger car and the petrol car, the effect of low average speed is much more pronounced for the petrol car. The reason is that the efficiency of a petrol engine drops much faster in part load than for a diesel engine.

When average speed on motorway drops from 120 or 100 km/h to values around 60 km/h, this usually does not increase fuel consumption, on the contrary. However real traffic jams, with standstill and low speed traffic (below 30 km/h), are usually at lower level speeds. In this case fuel consumption will clearly rise. So measures which lower average speeds at motorways to e.g. 80 km/h (like "block-driving" in Belgium) aiming to avoid traffic jams are also very efficient for fuel saving.

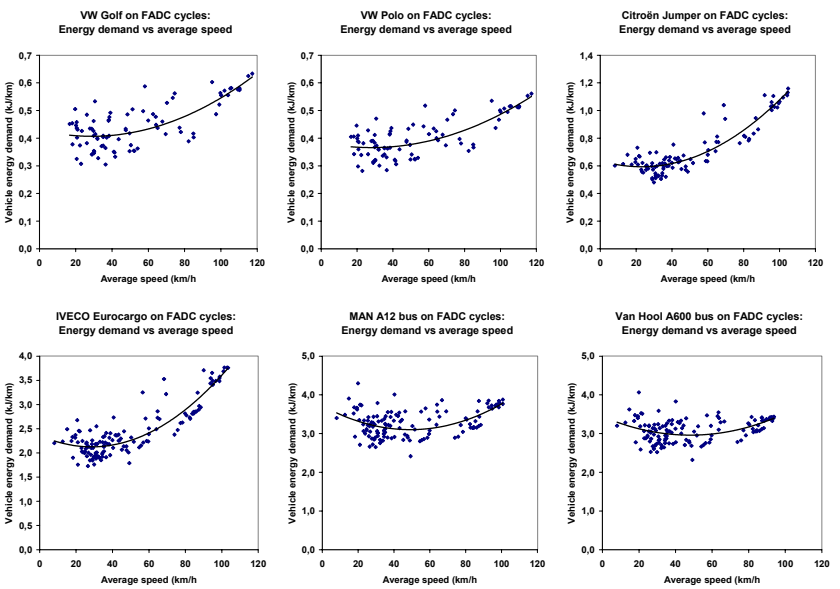

Figure 3: Energy demands calculated for the various recorded speed profiles as a function of average speed.

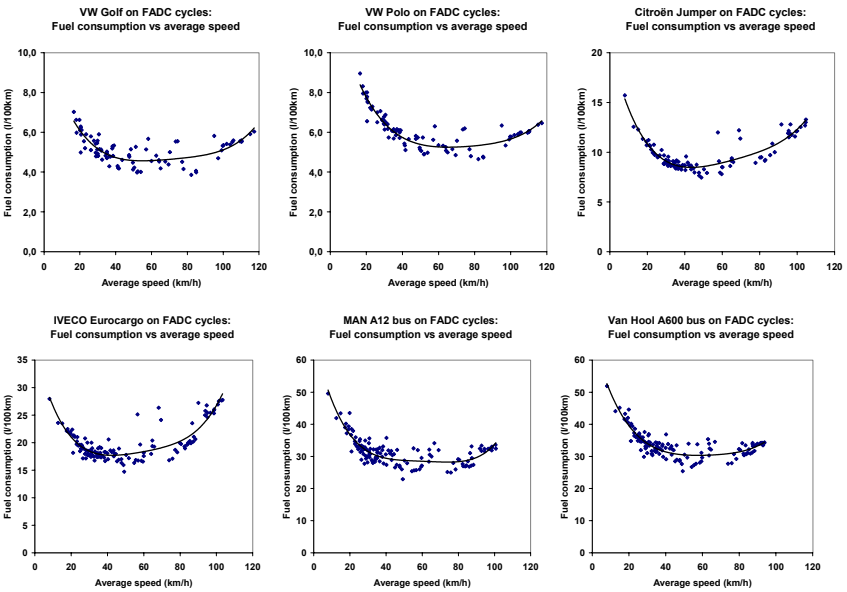

Figure 4: Fuel Consumption calculated for the various speed profiles as a function of average speed.

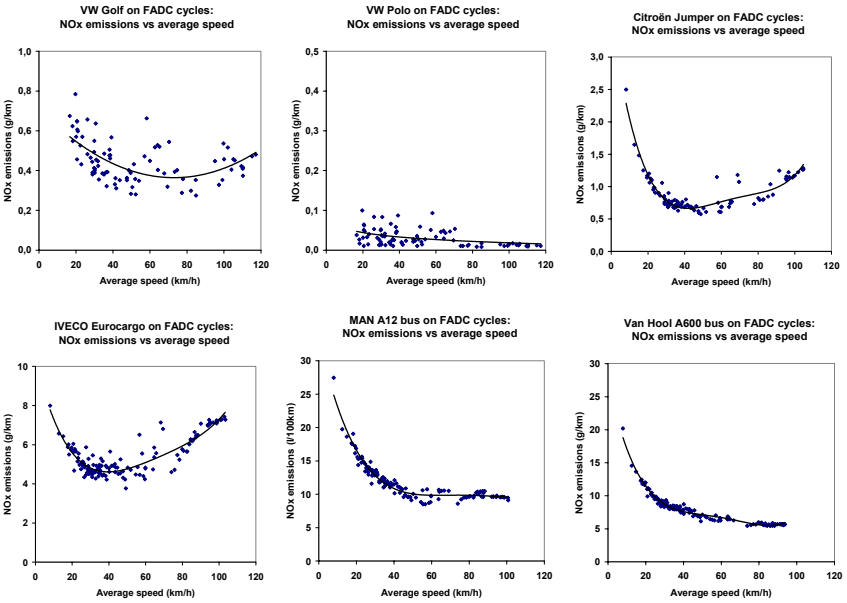

Figure 5: NO_x emissions calculated for the various speed profiles as a function of average speed.

3.4 Emissions

NO_x emissions are related to engine load, but some engine control effects (like EGR) do play a role. For gasoline engines there is the presence of a three-way catalyst which is most important for NO_x reduction, so the effect there is different, and NO_x emissions are generally much lower than for diesel vehicles. Concerning the diesel vehicles, in the following graphs it is clear that the increase in NO_x emissions at lower average speed is much more pronounced than for fuel consumption. Below average speeds of 30 km/h there is a substantial increase of average NO_x emissions.

Above certain speeds, again there can be an increase of NO_x, however less pronounced than for the lower speeds.

While NO_x emissions for the gasoline car are much lower than for diesel cars, for CO emissions it is totally different.

The high speed effect is much less for CO emissions; at lower average speeds there is a clear increase of CO emissions, especially when looking at the results for the buses and the truck.

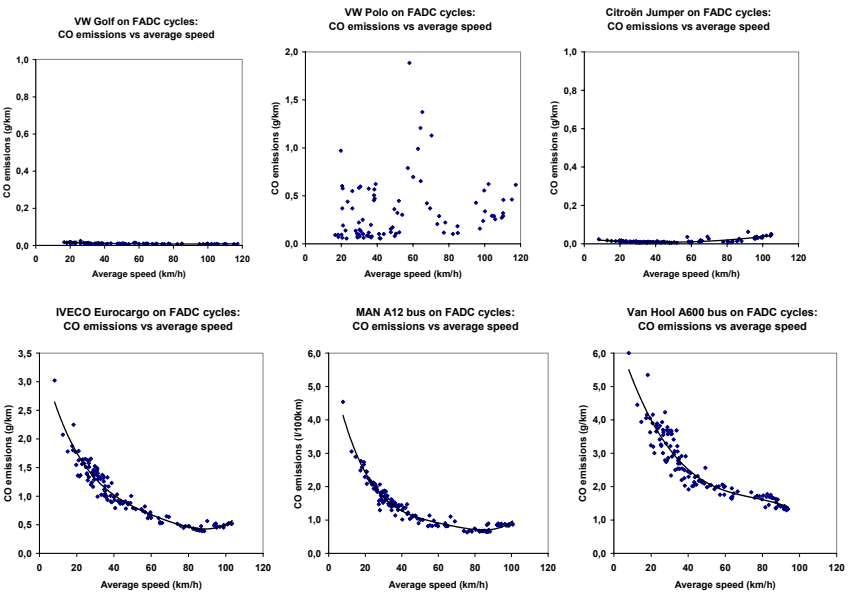

Figure 6: CO emissions calculated for the various speed profiles as a function of average speed.

For HC emissions conclusions are similar to CO, so graphs are not included here.

The effect of lower average speeds is less pronounced for PM emissions. Overall some increase of PM at lower speeds can be noticed.

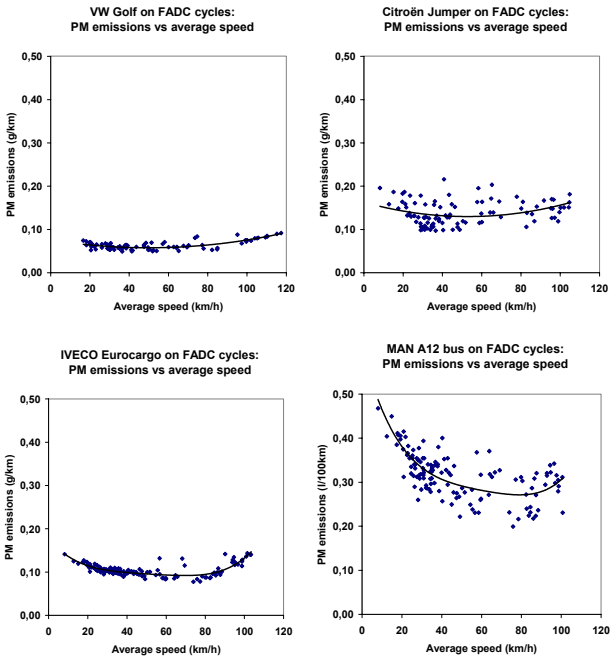

Figure 7: PM emissions calculated for the various speed profiles as a function of average speed.

4 Conclusion

From the simulations it was concluded that a reduction in average speed does not necessarily lead to higher fuel consumption. Actually when talking about high speeds (above 100 km/h), fuel consumption rises with higher average speeds.

When talking about traffic jams, it is the low average speeds which matter. When dropping below 30 or 40 km/h in average speed, it was indeed noticed that fuel consumption increases significantly. Emissions of NO_x, CO and HC also increase when speed drops below 30 or 40 km/h.

Concerning fuel consumption and emissions it is indeed worth the effort to prevent traffic jams and slow traffic and to improve the traffic flow.

The role of traffic jam detection is very important to take measures to improve the traffic flow and this way save fuel and reduce emissions.

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Modelling vehicles kinematics and parking processes relevance on pollutant emissions in the city of Florence

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Abstract

The new version of TEE model (Transport Energy Environment) has been developed in the frame of the FP5 ISHTAR and HEARTS Projects with several features for better analysing transport related direct impacts, taking into account vehicles kinematics, cold start emissions distribution, parking processes, noise emissions and accident occurrence. Specific efforts were dedicated to the modelling of the effects of vehicles kinematics on hot emissions, where the software calculates link emissions by adopting average speed based functions, instantaneous emissions, or the innovative 'kinematics correction functions' model, and the modelling of parking processes which are relevant for cold start and evaporative emissions. In the frame of the testing and the application of the software version developed in the HEARTS Project, the tool was applied for the analysis of the effects of various transport measures in the city of Florence. The assessment of TEE software was performed in conjunction with a well-known dispersion model (OSPM) and the collection of air pollution measured data. The results obtained have shown the greater accuracy and sensitivities that can be achieved through the detailed modelling of key processes affecting vehicles emissions. Details of these results will be presented in the conference.
Keywords: transport policies assessment, vehicle emissions, urban planning, vehicle kinematics, parking.

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1 Introduction

Emissions from transport vehicles are modelled in a number of different ways, but this variability includes some 'fundamental rules' that give the 'essence' of emissions calculation: emissions are the sum of at least two main components: 'hot emissions' and 'cold start emissions'. If the modeller is interested in VOC emissions, then also the 'evaporative term' has to be added. Hot emissions are the emissions emitted when engine and abatement devices have reached a regime temperature. They are influenced by a number of parameters: vehicle kinematics, gradient of the road, altitude, maintenance level, vehicle age, vehicle loading, and electric loads. Normally models refer to hot emissions as a function of kinematics (e.g. average speed or instantaneous speed and acceleration) and then multiply the 'ideal' hot emission value for a number of corrective factors taking into account the other mentioned parameters (Negrenti [1]). Cold Start emissions are the emissions emitted from the start up until the vehicle reaches an almost steady state thermal condition. The cold start emissions affect in practice the first 3 or 4 kms of trip and are particularly relevant for catalyst vehicles. Evaporative emissions are the emissions of unburned fuel from the 'weak points' of the vehicle: tank and canister. Current classic modelling recognises three different contributions to evaporative emissions: a) 'running emissions', emitted when vehicles are driven (emissions at tank level), b) 'hot soak' emissions, emitted from the canister at trip conclusion, and 'diurnal emissions', emitted at tank level by vehicles already parked. Evaporative emissions are a relevant fraction of total transport related VOC emissions, and so have a major role in the planning of measures for reducing VOC related pollution (e.g. critical benzene air pollution in Southern European cities). Two fundamental paths for increasing the accuracy of link based emission models are the more realistic modelling of vehicle kinematics and parking processes.

2 Methodology

The new version of TEE model (TEE-2005) allows to better analyse transport related direct impacts, taking into account vehicle kinematics, cold emission distribution, parking processes, noise emissions and accident occurrence (Negrenti [2]). As it regards vehicles kinematics, TEE calculates link emissions by adopting different options: average speed based emissions, instantaneous emissions, and the innovative 'kinematics correction functions' model describing both traffic flow condition and vehicle behaviour. The adoption of the kinematics correction has given very good results in the prediction of CO concentration levels in the city of Rome. For cold start emissions distribution, TEE now offers alternative solutions based on defaults of cold percentage depending on area type and day hour, or on the user input of either a link based cold fraction or the link related driven distance from trip origin. The parking process sub-model provides a meaningful treatment of traffic flows from and to parking areas and so allows one to better locate cold start vehicles emissions and evaporative emissions in space and time. The software now includes two fully

new models: the noise emission model and the accident occurrence model. The former is sensible to vehicle speed and heavy duty vehicles presence. The accident model calculates the number of accidents involving only vehicles or vehicles and pedestrians and splits them by severity. These new models broaden the scope of TEE software from pure 'consumption and emissions' modelling to the area of the direct impacts of transport systems.

One of the most relevant developments for the accurate estimate of pollutant emissions distribution at urban level is the realisation of an 'advanced parking model'. Parking policy plays an important role (Hoglund [3]) in the traffic system and it affects the level of traffic congestion and environmental quality in most cities. This work focuses on a specific parking model for the accurate determination of emissions due to parking inlet and outlet processes as represented within the TEE modelling framework. The TEE model link representation is characterized by three 'flow modes' corresponding to transit, parking and inserting vehicles. The behaviour of the parking and inserting flows is described by means of simplified speed cycles, based on the kinematics of the vehicle during the parking and the insertion phases. The main parameters defining the shape of these cycles are searching speed, searching time and warm up time.

Parking search phase was represented in this work by dedicated 'searching speed' and 'searching time' models. The first model estimates searching speed (Young [4], Zadeh [5]) through a fuzzy approach as a function of the mean linear vehicle density and the occupation rate of the parking facility. The second model (Anderson [6], Van der Waerden et al [7]) uses a probabilistic approach to calculate the searching time based on the occupation rate of the link connected parking areas. The searching speed model and the searching time model are further divided into two sub-models depending on the category of parking: on-street and off-street. As it regards the inserting phase, a large amount of pollutants is emitted due to the cold start effect. A set of models have been proposed in order to calculate the time employed by a car to be fully warmed up. Applications of the models showed that the parking model approach improves the sensibility of the TEE software. These specific models were integrated in the TEE 2005 Model in the framework of the EC FP5 HEARTS Project, and applied in the city of Florence by the ARPAT team.

3 Model development and application results

The two main developments recently obtained are here discussed: the kinematics modelling for transit flows and the modelling of parking.

One of the promising alternatives to the classically 'macroscopic' average speed emissions approach aims at obtaining a reasonably adequate kinematics description on the basis of easily available input data: the link average speed itself, a congestion indicator such as the 'lane flow density', link length and the fraction of green time at the intersection at the end of the link. The traffic density is used for calculating the fractions of time spent during cruising, acceleration, deceleration and idling phases. For low densities, traffic is smooth,

very limited interactions occur among vehicles and all the time is spent in the cruise phase. For higher density values accelerations induced by interactions start, thus reducing time available for cruising. When density exceeds a threshold value, spontaneous breakdown occurs and short idling events take place. As density finally approaches the upper limit value we observe a fast decline of cruise time, a progressive reduction of time spent in accelerations and the rise of idling time until traffic is blocked at the density saturation value. The time spent during acceleration and deceleration is used to estimate the number of acceleration episodes on the basis of a driver behaviour hypothesis and acceleration rates derived from measured data. The minimum speed along the speed cycle can also be calculated from these data. The knowledge of the average speed and the time spent in cruising and in the other driving phases allows also the cycle cruising speed to be calculated. The overall result is a 'reconstructed' speed profile characterised by: a time interval spent in idling (only for high densities or presence of a traffic light), some accelerations and deceleration episodes between the minimum speed and the cruise speed, and a time interval spent at 'cruise' speed. This relatively simple solution describes the likely speed cycle far from the traffic light that is supposed (if any) at link end. The 'Kinematics Correction Function' (KCF) Model makes extensive use of the 'reconstructed cycle' algorithm. This approach assumes that the effect of speed variability can be expressed by means of a 'kinematics correction function'. The 'corrected' emission 'E' is obtained as the product of the 'average speed emission 'e' and the 'kinematics correction factor'. The KCF can be derived from a set of emission calculations in which both the 'reconstructed cycle' model and the average speed correlation are used. In order to derive a function of general applicability, the authors had to define a matrix of possible traffic conditions. By considering a discrete number of average speeds, of 'green time percent', of congestion levels represented by traffic density, and of different link lengths, it was possible to define a four-dimensional matrix of theoretical traffic situations for which the fuel consumption and the emissions of CO and VOC were calculated with both the approaches. This way the influence of the speed cycle can be quantified and the characterisation of the KCF as a function of speed, density, green time fraction and link length can be performed. The matrix used in the most recent recalculation of the KCF includes over 1300 different traffic conditions. The correlation between the KCF and the four input parameters was searched as the product of four independent functions:

$$KCF = K0 * d(D) * g(G) * l(L) * v(V) \quad (1)$$

where d, g, l, and v are classic mathematical functions of the variables D (traffic lane density, in vehicles/km), G (green time fraction), L (length, in km) and V (Average Link Speed in km/hr), and K0 represents the value of the KCF coefficient for 'central' values of the four input variables.

TEE model adopting this correction function was assessed against CO measurements in Rome in the frame of the FP5 HEAVEN and ISHTAR Projects.

Estimated CO levels were compared with the measured values in the Viale Libia monitoring station. Significant differences were found between the use of the KCF correction and the simple use of the COPERT III functions for hot emissions. The use of the correction largely provided the best results.

The daily profiles were predicted with very good approximation. The correlation of data calculated and measured was remarkably high (0.85). The calculated CO level without the adoption of the KCF correlation would have been sensibly lower (for the case of CO the KCF function ranges normally between 1 and 3).

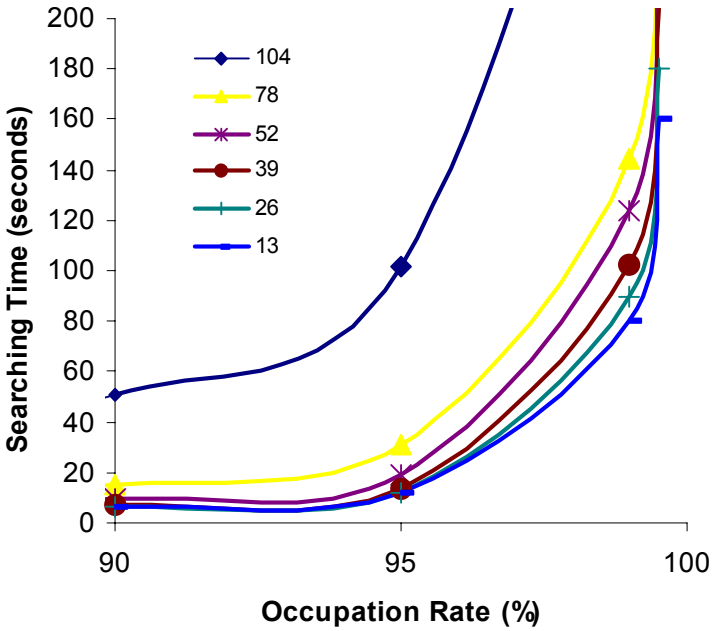

Figure 1: Searching time as a function of occupation rate for several densities.

The model of the searching time is then based on the analysis of probability number of attempts that a driver must carry out before finding a useful place to park. Relationship of searching time is the following:

$$T_{searching} = \mu \frac{L_p}{V_{searching}} = \frac{L_p}{V_{searching}} \cdot \frac{N+1}{occ_2 - occ_1} \cdot \log\left(\frac{N+1-occ_2}{N+1-occ_1}\right)$$

where μ is the mean value of attempting, N is the total parking places, L_p is the length of considered parking place, occ_1 is the number of occupied places in the beginning of the interval of study, occ_2 at the end of interval and $V_{searching}$ is the speed of search.

From parking model application a dependence emerges among the occupation rate, the searching time and the vehicle density. Searching time grows very slowly up to occupation rate of 95%, then it increases quickly to a maximum value achieved when then parking is full.

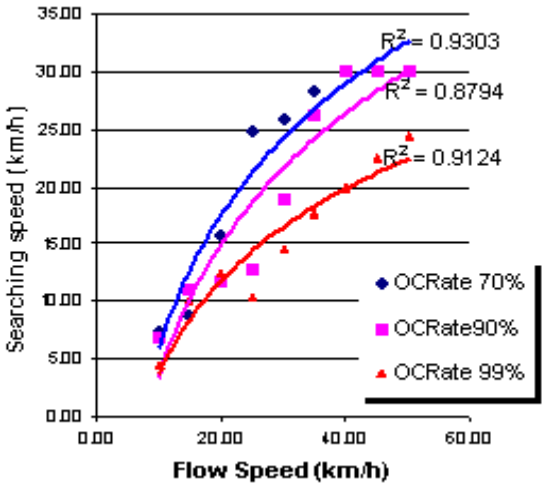

Figure 2: Search speed as a function of link speed and occupation rates.

To run TEE emission model it is necessary to complete the information obtained from traffic model EMME2 used in Florence. We need the traffic flow for the other hours of the day (hourly profiles) and the traffic flow for the other travel modes (i.e. two wheelers, duty vehicles, tourist coaches and extra-urban buses etc.). Moreover we need some data relating to the geometric characteristics of the links (e.g. link length, mean slope of link, etc.) and other data on traffic type of the link (link class, location and timing of traffic light, link area type, availability of parking and number of parking places etc.). In Table 1 we show the main information required for the application of TEE, with a short description of source of data used in the applications for the case study. Also, we denote the importance and the reliability of data (expert judgement). We point out that for some information the importance is different for the KCF (kinematics correction) or VM (average speed mode) options of TEE model. Each link has been classified according to traffic road categories. We used five road categories:

1) town entry/exit main roads
2) internal main roads
3) secondary roads in ZTL (controlled traffic zone, in the town central area)
4) secondary roads
5) highways and similar roads

Table 1: Summary of the data used in TEE application.

data	Source	reliability	importance
flow	EMME2 output+measurement	to test	high
speed	EMME2 output+measurement	to test	high
lanes	EMME2 output	good	high (KCF) , low (otherwise)
length	GIS calculation	good	high
slope	GIS calculation	good	low
fleet composition	measurements (macro) + statistical data and local corrections	good	high
cold start percentage	estimate from mobility data	low	medium
parking and inserting flow	calculation from EMME2 output + estimate	low	medium
properties of distributed and concentrated parking areas	data from local authorities + estimate	low	medium
traffic lights: cycle and green percentage	Default	low	medium (KCF), nothing (otherwise)

For each road category we know the hourly profiles of total vehicular flows; from direct measurements on sample roads we estimate the subdivision of total flows in sub-flows of macro-classes of vehicles. The number of vehicles belonging to micro-classes is obtained by splitting the total flow of a macro-class into single micro-classes flows according to the "weight" of the micro-class.

The mean speed at each hour is obtained from a flow-speed curve for each road category. In the lack of specific data from traffic model, the rate of cold start vehicles is estimated from mobility conjecture and data. For each link (and each hour of day) the cold fraction of vehicles is randomly drawn from a suitable range (with statistical uniform distribution). This range is obtained considering the length of daily mean trip, the total number of daily travels, the number of cold daily travels and the mean cold trip length. The rates of the inserting and parking vehicles on each link are estimated by processing output data of the traffic model. On each node of the network we calculated the balance of input and output vehicles from all the links connected to the node. The node is defined as "parking" or "inserting" whether input vehicles are larger than outgoing ones and vice versa. For parking nodes, the difference between input and output

vehicles divided by the total number (input+output) of vehicles yields the percentage of parking vehicles assigned to the node considered. For inserting nodes we used the difference between output and input. It is clear that these values are a lower bound for link parking (inserting) vehicles. In addition to these data, a fixed rate for both inserting and parking vehicles is assigned to each link of the network. We have geo-referenced in a GIS framework the main concentrated parking areas of Florence town, with the related properties (number of car places, mean time of parking, hourly percentage of filling up etc.) obtained from data given from the local authority and management. Finally we have assigned link parking places by GIS calculation routine. For the policy scenario 'year 2010' we have used again the methods described above and many data were kept at the level of those of current scenario 'year 2003'. In synthesis, the most important changes in the forecast fleet are the insertion of future new micro-classes of vehicles according to EU standards and the very high reduction of the old 2-strokes mopeds (PRE EURO) with the increase of 4-strokes motorbikes; for the existing old micro-classes of vehicles at year 2003 (i.e. PRE EURO, EURO1, EURO2) we have assumed the reduction to be proportional to the number of vehicles in the micro-class, then we have used a yearly rate of reduction as the one between years 2002 and 2003. We have in general assumed to keep the same number of vehicles for a given macro-class.

Finally we tested the emission results of TEE KCF option and TEE "average speed" option. We compared the CO concentrations measured in an air quality monitoring station with the concentrations estimated by a dispersion model. We used the OSPM street canyon model (NERI, Denmark, OSPM 2000). The emissions provided by TEE KCF mode and TEE VM mode are used as input for the dispersion model. As an example, in Figure 3 and Figure 4, we show the hourly CO concentrations measured by the monitoring station and the OSPM results. The agreement between modelled and measured concentrations seems to be very good with KCF mode, but we have to take into account also the background concentration that is estimated to be about 0.5 mg/m³. For the same reason the difference between measured and 'average speed' option concentrations is not so big as shown. These results suggest that in the specific application of TEE emission model, the emissions from the real traffic on the street are inside a range between the two options of TEE model. In any case we recommend to run sensitivity studies on the most impacting uncertainties as those on the fraction of cold vehicles, the effects of vehicles aging, the poor knowledge of fleet composition for some categories. The consideration of the related variability can in facts significantly modify these conclusions.

4 Conclusions

New approaches have been developed for describing the effects of vehicle kinematics both in the transit flows and in the parking processes. These new models reduce the uncertainties in the description of the spatial and temporal distribution of emissions in all its main components : hot, cold start and evaporative. The application made in the city of Florence gave positive

indications on the higher accuracy and sensitivity reached, but also suggested further areas of investigation and reduction of uncertainties for vehicles emissions modelling.

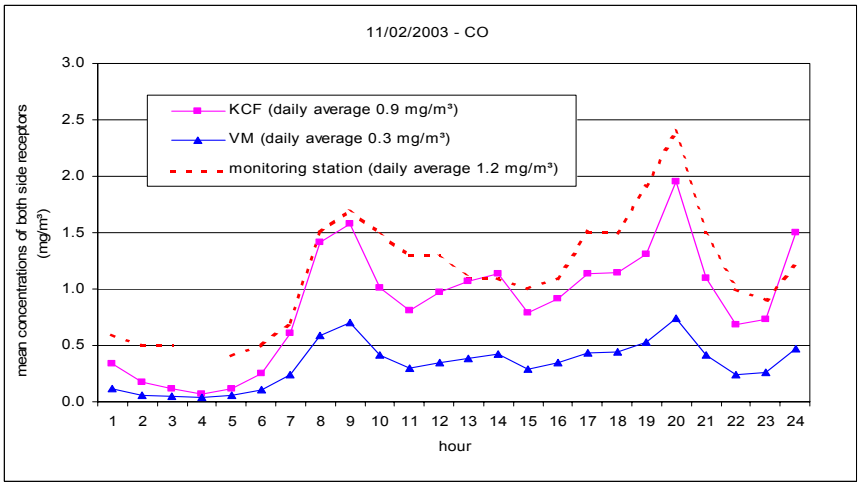

Figure 3: Hourly CO concentrations (February 2003) measured by an air monitoring station and those modelled by OSPM model and TEE with KCF (top) and average speed (bottom) kinematic options.

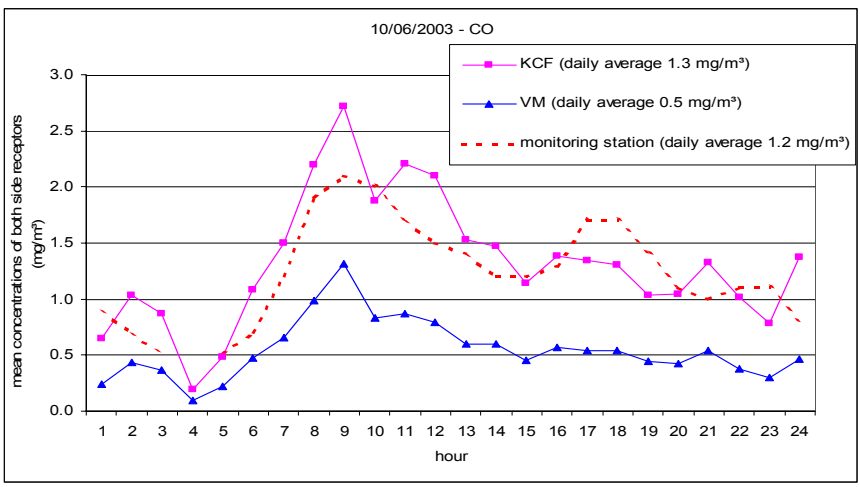

Figure 4: Hourly CO concentrations (June 2003) measured by an air monitoring station and those modelled by OSPM model and TEE with KCF (top) and average speed (bottom) kinematic options.

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Section 5
Monitoring and laboratory studies

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Biological monitoring – the useful method for estimation of air and environment quality

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Abstract

Bioindication with different bioindicators (lichens, mosses, tree leaves and small mammals) has been used for thirty years (1975–2005) to estimate air pollution and environment contamination in Poland. Air contamination by heavy metals and sulphur dioxide in the Base Station of the Environmental Nature Monitoring System and in 23 Polish National Parks was estimated using lichen *Hypogymnia physodes* as a bioindicator. The impact of the Kraków conurbation and the contamination of forest ecosystems, using tree leaves and small mammals, were evaluated, respectively. Biological monitoring showed the changes of environment quality in Poland but also confirmed the presence of some areas still being contaminated. They are located in different parts of Poland also far from industrial sources.
Keywords: Poland, environment, biomonitoring, air pollution, heavy metals, sulphur dioxide, lichens, mosses, higher plants, small mammals.

1 Introduction

Chemical compounds which have caused organisms' and environmental stress were released into the environment as a result of human activities. The pollution originates mainly from industrial manufacturing and energy production, coal and oil combustion (industrial and residential), vehicular traffic and also small local sources. In the last few decades the main sources of pollution in the whole Europe have been increasing urbanisation and heavy traffic [1–3]. Biomonitoring – a very useful, sensitive and effective biological method to assess air pollution or to estimate contamination of natural environment – has been used for more

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than 50 years [4–7]. Biological monitoring is the measurement of the response of living organisms to changes in their environment [8]. According to other authors biological monitoring is the measurement, usually repeated, of concentrations of environmental contaminants in free-living organisms, or the measurements, either singly or in combination of changing of genetic, biochemical, physiological, behavioural and ecological parameters [9]. Generally lichens, plants and animals can be used as bioindicators. Several classifications of bioindicators are used. The simple one recognizes only two groups: monitors and indicators [10]. More complicated divide them for five groups: sentinels, detectors, exploiters, accumulators, bioassay organisms [11]. Biomonitoring can be used at national, regional and local scale but can also be used to compare the environmental contamination between various countries.

Poland used to be one of the most polluted countries in Eastern Europe – for many years taking one of the first places in sulphur dioxide, nitrogen oxide and dust emissions [12]. Country was heavily affected by gaseous and particulates emissions (including heavy metals) originating partly from our local sources, and partly from long distance transport, mainly from west direction. The situation has significantly improved during the last seventeen years, but still most of the natural environment is heavily contaminated. In 2004, Poland emitted 443 thousands tonnes of dust, 1241 thousand tonnes of sulphur dioxide, 804 thousand tonnes of nitrogen dioxide. Heavy metal emissions also decreased when compared with early nineties but in 2004 Poland emitted 1597 metric tonnes (t) of Zn, 600 t Pb, 46 t Cd, 20 t Hg, 54 t Cr, 249 t Ni, 389 t Cu [13]. At the present time the main sources of emissions are not the heavy industry but small towns, large conurbation, heavy traffic, and small local sources. In the most cities airborne metals, gaseous pollutant and organic compounds (e.g. PAHs) are not routinely monitored with fully or semi-automatic gauges commonly used in pollution monitoring programs, owing to elevated costs and technical difficulties. In this situation biological monitoring is the important method to study the quality and distribution of contaminants.

The aim of this paper is to show the role of biological monitoring in studying changes in contamination of natural environment in Poland during thirty years using different bioindicators.

2 Material and methods

Bioindicator samples (lichens, plants and animals) from natural environment were collected all over the Poland during thirty years (1975-2005). The investigated areas were located in different polluted parts of the country, around the heavy industry steelworks, metal smelters, coal and metal mining, busy road, small urban area and Cracow and Warsaw conurbations. Samples were also taken from different forest areas, national parks, and Base Stations of the Integrated Nature Monitoring System for Poland. Unwashed lichens, mosses, plant, leaves and animal tissues were dried to a constant weight (at 60-70˚C) and digested in a 4:1 nitric and perchloric acid. In all samples concentration of heavy metals: Cd, Pb, Cu, Zn, Fe, Ni, Cr, V (depends from the study) and S were

determined. In case of metals, atomic absorption spectrophotometer flame or graphite furnace was used [6, 14], whereas sulphur content was determined using turbidimetric Butters-Chenry's method [15]. Simultaneously reference materials (SRM) were also analysed. Data are presented in $\mu g \cdot g^{-1}$ dry weight. Statistical analysis was carried to determine potential differences between the concentration of contaminants between sites and period of time.

3 Contamination of the environment in Poland

3.1 Lichens as monitors of air pollution

Lichens, the symbiotic association between fungus and alga, have been shown to be highly sensitive to gaseous air pollution, particularly to sulphur dioxide. They are very good indicator of this type of pollution. Lichens are generally insensitive to toxic effects of trace metals and can therefore be used as accumulator to estimate concentrations of these elements in the environment. They absorb substances for growth and survival through the exposed surface of the thallus. Epiphytic lichens growing on the tree stems and branches use them only as a substrate. Instead lichens get nutrients from rainwater and deposited dust. Along with the essential nutrients, they absorb many nonessential or harmful substances as well [16]. Lichens show the concentrations of metals and sulphur and organic compounds as a function of the amount of atmospheric deposition amount. Thus it makes them widely used in monitoring of air pollution [7, 17, 18]. They could be collected from natural environment or transplanted from clean area to the polluted sites [19, 20].

During 1997–2003 three different investigations (case studies) using epiphytic lichens *Hypogymnia physodes (L.)Nyl.* were carried out.

3.1.1 Contamination of Polish National Parks by heavy metals and SO_2

Samples of *Hypogymnia physodes* from natural environment were collected in July 1998 and 2003 from 23 Polish National Parks, Figure 1. The aim of this study was to estimate air pollution by heavy metals: Pb, Cd, Cu, Zn, Fe (Figure 2) and sulphur dioxide and to compare the contamination over period of 5 years [21]. Lichens from Ojcowski National Park situated in heavily industrialised region, had the highest concentration of all heavy metals. The lowest content of Cd, Pb and Zn were determined in Drawienski NP while the concentration of Cu and Fe were found in Białowieski NP. The highest concentrations of S were detected in lichens from Ujście Warty NP. As far as heavy metals, thirteen national parks were clean with very low pollution detected, nine represented moderately polluted areas and one was contaminated. In the case of SO_2, nine national parks were classified as clean; seven were recognized as moderately polluted, fifth as polluted and two were heavily polluted. Generally, national parks located in southern part of Poland were more contaminated by heavy metals than those in the north of the country.

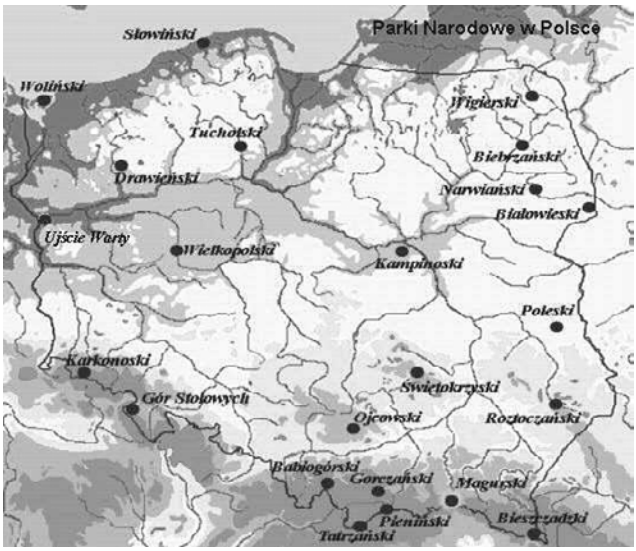

Figure 1: Localization of National Parks in Poland.

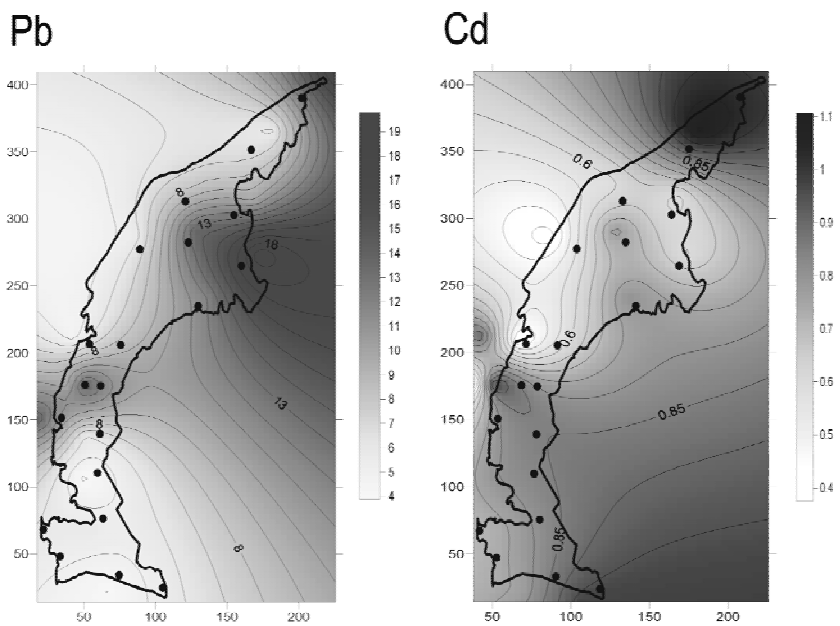

Figure 2: Lead and cadmium concentration ($\mu g \cdot g^{-1}$ d.w.) in the air of the Woliński National Park.

Contamination of sulphur dioxide is much more uniform across the country and reflect rather local sources of emissions and long distance transport than the

main industrial sources. Comparison of environment condition after a five-year period showed that heavy metals and sulphur concentration was not much lower as was expected. Only in case of copper and iron the concentration was lower than five years ago. Zinc represents the same level. Lead concentration was slightly higher or remained on the same level. Cadmium concentration was higher than five years ago. Sulphur dioxide in Polish national parks has not decreased compared to 1998, as sulphur concentration is much higher than five years ago.

3.1.2 Air pollution in the Base Stations of the Integrated Nature Monitoring System

Air contamination by heavy metals and sulphur dioxide in Base Station of the Integrated Nature Monitoring System was estimated using *Hypogymnia physodes* as bioindicator [22]. In July 2001, lichen samples from natural environment were collected in all 7 Base Monitoring Stations (Szymbark, Św. Krzyż, Pożary, Storkowo, Koniczynka, Puszcza Borecka, Wigry) and determined for concentration of heavy metals (Cd, Pb, Cu, Zn, Fe) and S. The highest concentration of both: all investigated metals and sulphur were found in Koniczynka Base Station situated nearby Toruń agglomeration. Also high concentration of cadmium, lead, zinc, iron and sulphur were noticed in lichens collected in St. Krzyż and Szymbark Base Stations. Global pollution Index and Sulphur Index showed different air contamination of studied Base Stations. The results of the following study confirmed air contamination by heavy metals and sulphur dioxide in three of the investigated Base Stations (Koniczynka, Św. Krzyż, Szymbark). During winter season 2002/2003 and summer season of 2003 *Hypogymnia physodes* from clean area were transplanted to those three Base Stations to find out the reason and sources of pollution. The data for summer transplantation showed the lower accumulation of all heavy metals with exception for Cd in Szymbark and Cd, Pb and Fe in Św. Krzyż (see Figures 3 and 4). Significantly lower accumulation was found for sulphur in lichens from all investigated Base Stations (Figure 5). The sources of emissions which caused contamination are different in the case of these three areas.

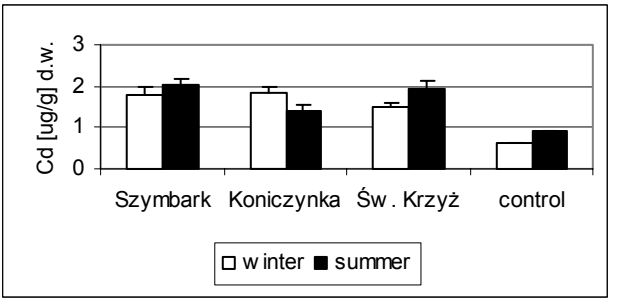

Figure 3: Cadmium content [$\mu g \cdot g^{-1}$d.w.] in lichens transplanted in the Base Stations.

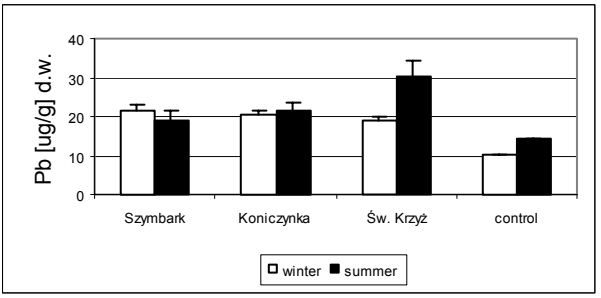

Figure 4: Lead content [$\mu g \cdot g^{-1}$d.w.] in lichens transplanted in the Base Stations.

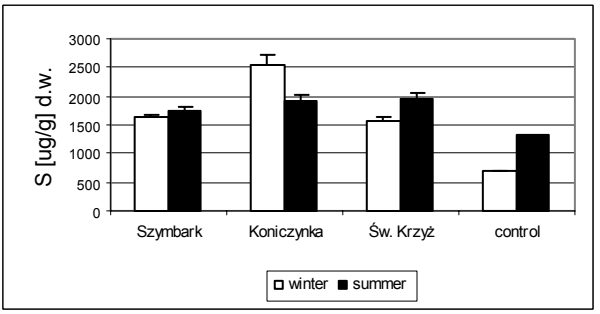

Figure 5: Sulphur content [$\mu g \cdot g^{-1}$d.w.] in lichens transplanted in the Base Stations.

3.2 Mosses as bioindicators of air pollution by heavy metals in Poland

Mosses accumulate large amount of heavy metals and therefore they are used as sensitive bioindicators of these contaminants in the environment [5, 8]. Mosses show the concentration of metals as the function of the amount of their concentration in air as they accumulate metals in the passive way [5, 23]. Another advantage that they are good bioindicator is that many moss species have a wide geographical distribution and are very common throughout the Europe. This is the reason that in EMAP two species of mosses *Pleurozium schreberi* and *Hylocomium splendens* were used as bioindicators of air pollution.

The first estimations of heavy metal contamination of the environment in Poland on a national scale, based on metal concentration in moss *Pleurozium schreberi* were conducted in 1975 in 12 Polish national parks [23]. The investigations were repeated in 1986, 1990 and 1995 [24–26].

In the project "Atmospheric Heavy Metal Deposition in Europe" the deposition of heavy metals in *Pleurozium schreberi* collected from 300 forest sites throughout Poland in 1990 and 1995 [26, 27]. Concentrations of seven heavy metals (Cd, Cr, Pb, Cu, Ni, Zn, Fe) in moss samples were analysed. The lower concentrations of all heavy metals were found in 1995 when compared with 1990 but despite these findings Poland is still the one of most contaminated areas in Europe [28].

3.3 Tree leaves as bioindicators of urban pollution

Tree leaves as the bioindicator of environment contamination were more frequently used in recent years, especially in urban areas [29, 30].

Seven forest sites that differed in their distance from Cracow conurbation and from busy roads were located along either southern or eastern transects and along the prevailing wind direction were selected. Five sites were located along southern transect (Bonarka located 3 km from the town centre, Rajsko 8 km, Mogilany located 14 km far from the city, Kornatka and Węglówka 26 km and 35 km respectively). Along the eastern transect only two sites: Koło (25 km from steelworks and 30 km from Cracow) and Ispina (30 and 35 km respectively) were located. Leaves from two tree species: hornbeam *(Carpinus betulus*) and oak (*Quercus robur)* were collected in the autumn for four consecutive years (1998-2001) from each forest sites [3]. High concentration of heavy metals (Cd, Pb, Cu, Zn, Fe) were detected in leaves of both species from eastern transect as the effect of steelworks emission, as well as in the sites from southern transect situated near the Cracow conurbation. Although the air pollution has generally declined in Małopolska district from the middle of nineties the metal concentration in tree leaves in 2001 remains at the same level than in the previous years [3].

3.4 Animals as monitors of environmental contamination

Animals, both invertebrates and vertebrates, have been used as bioindicators to assess environment contamination [9]. In many countries, small mammals have been used in assessment of heavy metal contaminations near smelters, mines, waste disposal sites, dumps, along the highways, [31, 32], see Figure 6. Small mammals are very useful monitors to estimate heavy metal concentration of forest, meadows or field ecosystems as they are closely adjusted to their environment.

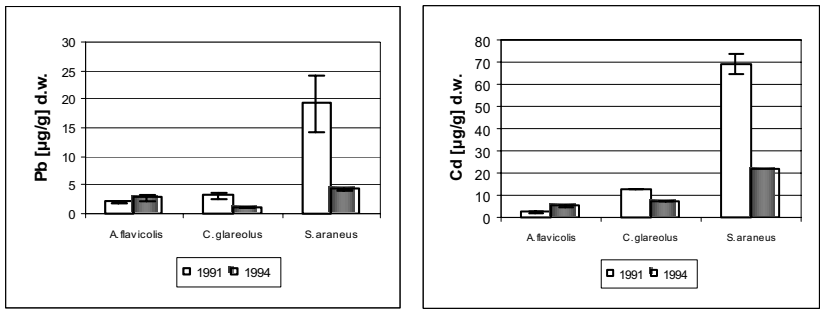

Figure 6: Lead and cadmium concentrations [$\mu g \cdot g^{-1}$d.w.] in the livers of small mammals from Olkusz Forest.

They are small enough and easy to catch. They have a territory of limited range and fairly short life span [9, 10, 31, 33]. In Poland, the levels of heavy metals in tissues and bodies of some rodents and insectivorous species were

analyzed for almost thirty years. Concentrations of heavy metals in tissues and bodies of small mammals vary with the degree of contamination [33–37].

4 Conclusions

1. Air pollution and environment contamination in Polish national parks have not decreased much during last five years.
2. Air contamination in Base Stations of the Integrated Nature Monitoring System was at average levels when compared with the whole country, due to elevated cadmium concentration and high concentrations of lead and sulphur in some of the stations.
3. Mosses used as accumulators showed that Poland is still one of the most contaminated by heavy metals areas in Europe.
4. Tree leaves are very useful bioindicators of urban pollution which was confirmed in the Cracow conurbation.
5. Small mammals were good monitors for estimating changes of quality and contamination of the natural environment in Poland.
6. Biological monitoring showed the changes of environment quality in Poland during thirty years but also confirmed the presence of some areas still being contaminated. They are located in different parts of Poland also far from industrial sources.

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Ambient air quality monitoring in southern Kuwait

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Abstract

Ambient air quality monitoring was conducted at twenty locations in the southern part of Kuwait as part of an environmental impact assessment study requested by the Kuwait National Petroleum Company. Two waves of passive samplers (triplicates) were used to measure: NO, NO_2, SO_2, H_2S, NH_3 and a high volume sampler was used to measure PM10. During the sampling period, the wind was observed to be predominately from the west and northwest with an average speed of 4.28m/s. A comparison between the measured concentrations and the applicable air quality standards promulgated by the Kuwait Environment Public Authority showed that those compounds had very low concentrations compared to both industrial and residential KEPA standards and accordingly there is no violation of KEPA air quality standards.
Keywords: passive samplers, air pollution, PM10.

1 Introduction

The Kuwait National Petroleum Company (KNPC) requested that the Kuwait Institute for Scientific Research (KISR) conduct a baseline Environmental Impact Assessment (EIA) study for building the fourth refinery in Az-Zour area in the southern part of Kuwait, which is shown in Figure 1. In this paper we report on the results of the ambient air quality monitoring part of the conducted EIA.

2 Sampling locations

Ambient air quality monitoring was conducted at twenty locations as shown in Figure 1. The UTM coordinates and description are listed in table 1. The

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monitoring locations include the planned New Refinery site, the coastal area adjacent to the planned marine terminal site, nearby residential areas and locations upwind and downwind of the Az-Zour North and South Power Stations (bounded by A7, A8 and A9).

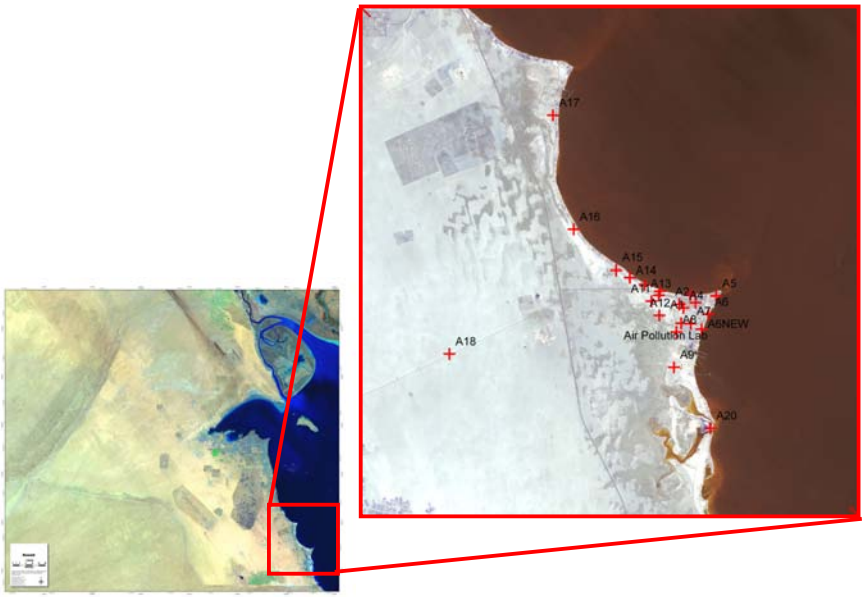

Figure 1: Locations of ambient air quality monitoring.

3 Monitoring techniques

Passive samplers (triplicates – refer to Figure 2) were used at twenty locations to measure the following components: NO, NO_2, SO_2, H_2S and NH_3. The samplers were secured to existing structures or on temporary supports. The samplers were deployed using a PVC rain shelter and incorporated support clips provided by the manufacturer (IVL Swedish Environmental Research Institute Ltd - Gothenburg, Sweden). Even in the absence of rain, the shelter is required to minimise dust contamination and the effects of advection on the diffusive samplers. Based on the passive samplers manufacturer's advice, the samplers were left in the field for 336 hours. Prepared samplers were transported to and from the field in air-tight containers, and minimally handled in the field using latex gloves. The passive samplers were then sent to IVL for analysis. Passive samplers were installed in two waves between 26/10/2005 and 24/11/2005.

During the sampling period, the meteorological conditions, e.g. wind speed and direction, relative humidity, precipitation, atmospheric pressure and temperature, were monitored using portable weather stations. The wind was observed to be predominately from the west and northwest with an average speed of 4.28m/s. From the windrose plot shown in Figure 3, it can be seen that

14% of the measured wind had an angle of 259° - 281°, 15% had an angle of 281° - 304°, 13% had an angle of 326° - 349° and 13% had an angle of 349° - 11°. Precipitation was recorded on 12th and 13th November 2005. The average atmospheric pressure and temperature 1014Pa and 22.4°C respectively and the average relative humidity was 56%.

Table 1: Locations of ambient air quality monitoring – based on 39 projection.

Location	X	Y	Description
A1	243627	3182158	Health Clinic Yard
A2	242897	3181526	Outside the fence of a school
A3	243991	3181641	The roof of the local police station
A4	243163	3181286	Open area close to village houses
A5NEW	241572	3182422	Near the beach
A6NEW	244402	3179826	Near the northeastern corner of Zour Power Station
A7	243665	3180202	Approximately 200m from Az-Zour North Power Station northern boundary
A8	242695	3179628	Approximately 200m from Az-Zour North Power Station western boundary
A9	242526	3177219	Approximately 200m from Az-Zour North Power Station southern boundary
A10	241494	3182145	New refinery boundary
A11	240993	3181745	New refinery boundary
A12	241528	3180770	New refinery boundary
A13	240524	3182861	Outside the first house in the beach village
A14	239521	3183360	1km from A13 outside the coastal houses
A15	238596	3183844	2km from A13 outside the coastal houses
A16	235706	3186621	4km from A15 outside the coastal houses
A17	234296	3194417	8km from A16 outside the coastal houses
A18	227250	3178135	18km from new refinery site, 200m away from roadside
A20	245001	3173056	Existing residence at Khiran Resort
APL	243015	3180239	Inside Az-Zour North Power Station fence

Figure 2: Triplicate set of the passive samplers.

A PM10 Volumetric Flow Controlled (VFC) high volume air sampler (VFC System – Model TE-6070V, Tisch Environmental Inc. – Ohio, USA, shown in Figure 4) was used to measure the PM10 levels at four locations (A3, A13, A17 and A20). The high volume air sampler uses Micro-Quartz filter (Model: Whatman-PN 1851-865 QM-A (8 x 10 inch)) with 99.95% particle retention (0.3μm) which is recommended for use in USEPA PM10 ambient air monitoring. The high volume air sampler was calibrated using a TE-5028 variable orifice calibrator for a pressure difference range of 12-19inch H_2O. At each monitoring location, the high volume air sampler was left on for nearly 24 hours and the total volume of air (actual and standard) passed through the filter was calculated to estimate the PM10 concentration.

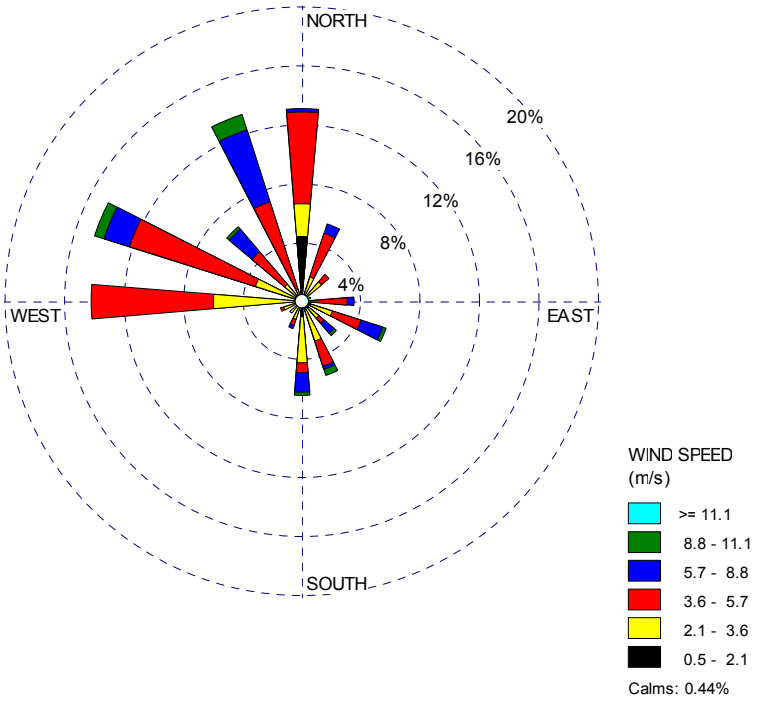

Figure 3: The windrose plot for the sampling duration.

Figure 4: The PM10 high volume air sampler in use at A17.

4 Results and discussion

- The contour plots for the concentrations obtained for NH_3, NO_2, NO, SO_2 and H_2S are shown in Figures. 5-9. The PM10 concentrations are shown in Figure 10. Table 2 lists the maximum, minimum and average concentrations detected by the passive samplers.

Table 2: The average, maximum and minimum concentrations measured and their locations.

Pollutant	Concentration (µg/m3)				
	Max	Location	Min	Location	Average
NH3	4.43	A9	2.53	A1 & A20	3.35
NO2	18.63	APL	7.43	A18	14.9
NO	14.1	A20	7.87	A18	11.48
SO2	16.4	A3 & A7	10.47	A17	13.24
H2S	7.8	A18	2.4	A10	4.53
PM10	90.47	A17	40.43	A3	67.93

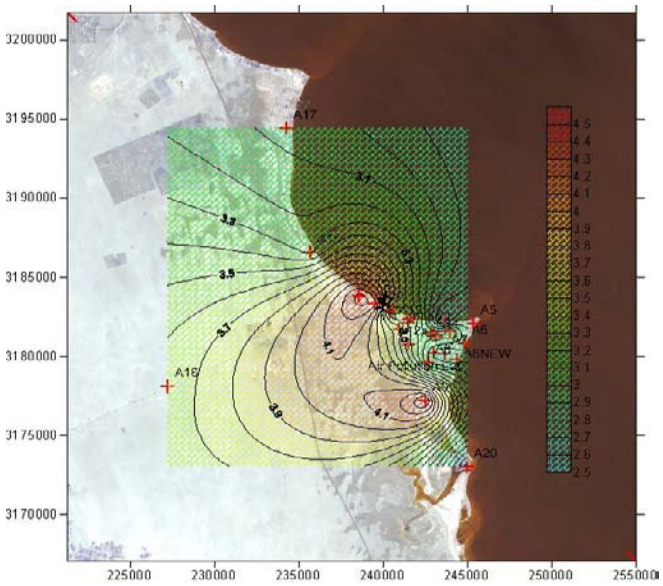

Figure 5: Showing the contour plot for the NH_3 concentrations.

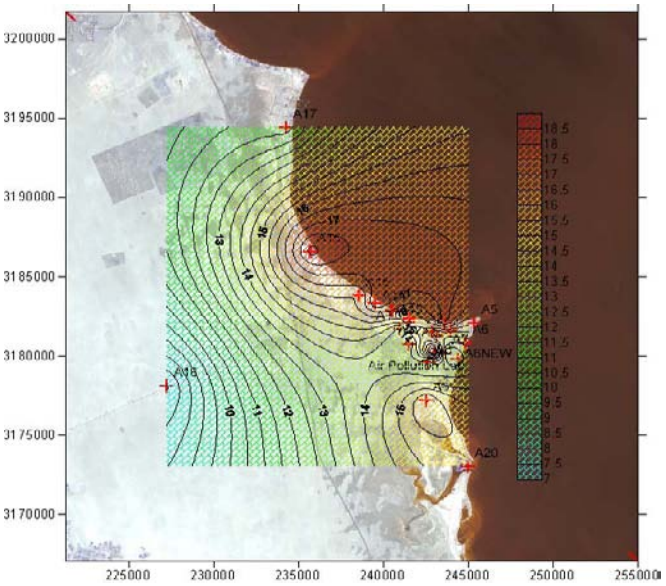

Figure 6: Showing the contour plot for the NO_2 concentrations.

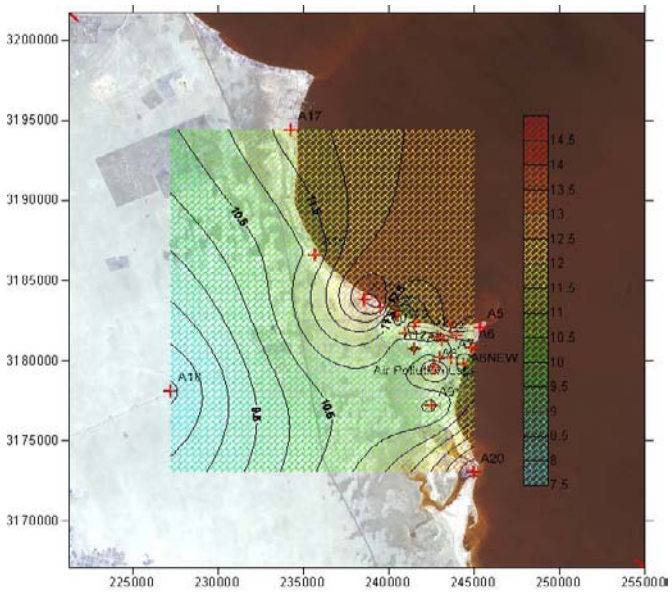

Figure 7: Showing the contour plot for the NO concentrations.

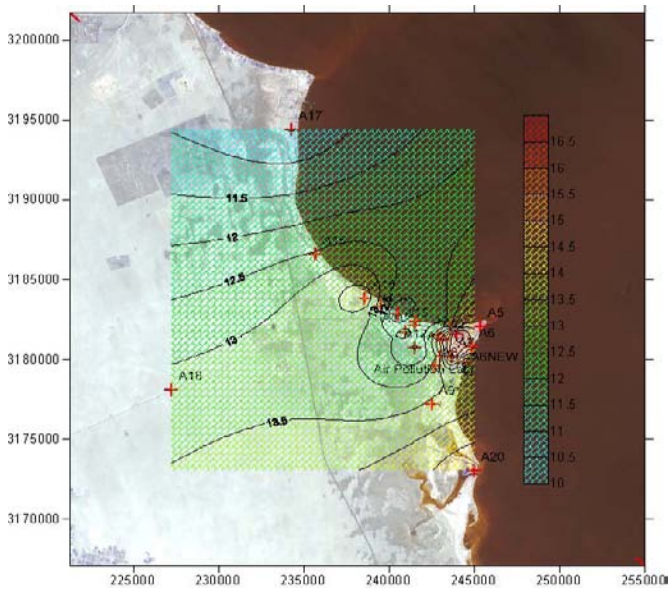

Figure 8: Showing the contour plot for the SO_2 concentrations.

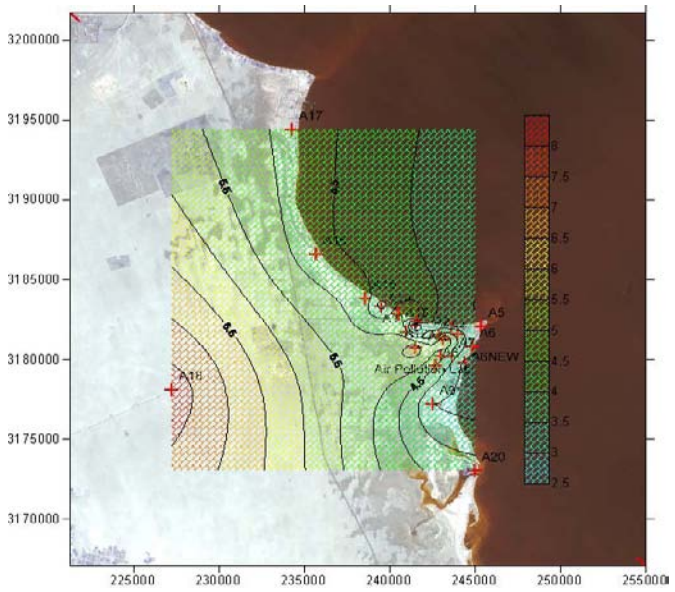

Figure 9: Showing the contour plot for the H_2S concentrations.

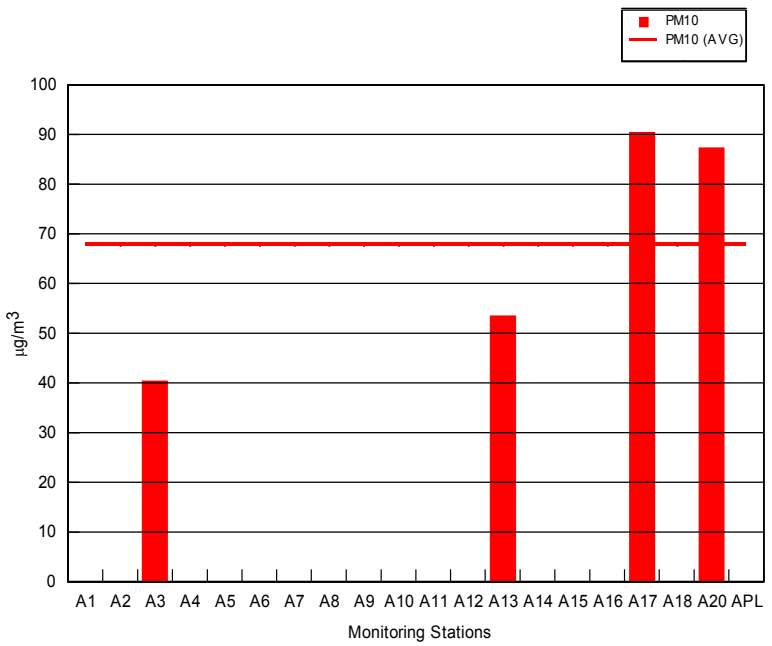

Figure 10: Distribution of the PM10 concentrations.

NH_3 concentration is highest at A9 and A15. A9 was near a landfill site while A15 was inside a farmhouse with poultry. Agricultural activities, in particular animal husbandry, are the dominant source of NH_3 emissions to the atmosphere, contributing an estimated 90% of the total in Western Europe (Sutton *et al* [1] and Kirchmann *et al* [2]) and the US (Battye *et al* [3]). The NH_3 concentration drops rather quickly as we move away from the A15 and A13.

NO_2 distribution is high in the north-eastern part of the area where the car traffic is higher and it decreases gradually with distance towards the south-eastern region. Low NO_2 levels at A17 and A18 are indicative of the rural setting of the south-eastern part of the area. The NO distribution is similar to that of NO_2 with the minimum concentration attained at A18, which is on the side of a rarely used road. The maximum NO concentration was measured at A20 near a car park inside a heavily populated resort.

The high SO_2 concentration at A3 and A7 is due to oil handling and transport facilities (pipelines, pumps, etc) associated with Texaco activities. The high SO_2 concentration at A20 is contributed to the plume of Az-Zour Power Stations, which is deflected under the prevailing northwesterly winds.

The H_2S concentration was highest at A18, which was 10m from a crude oil pipeline. The PM10 measurements were not made at the same time; hence the concentration levels cannot be related to the locations. However, the high PM10 concentration at A17 can be related to the off-road driving activities on the measurements day.

A comparison between the measured concentrations and the applicable air quality standards promulgated by KEPA shows the following:

1. The maximum measured concentration ($4.43\mu g/m^3$) of NH_3 is negligible compared to all the KEPA residential and industrial standards for NH_3.
2. The maximum measured concentration ($18.63\mu g/m^3$) of NO_2 is less than one third of the KEPA yearly standards for both residential and industrial areas for NO_2.
3. The maximum measured concentration ($16.40\mu g/m^3$) of SO_2 is about one tenth of the yearly KEPA industrial standard and one fifth of the yearly KEPA residential standard for SO_2.
4. The maximum measured concentration ($7.80\mu g/m^3$) of H_2S is less than the yearly KEPA standard for residential areas for H_2S.
5. The maximum measured PM10 concentration ($90.47\mu g/m^3$) is less than one third of the daily KEPA standards for both residential and industrial areas for PM10.

5 Conclusion

The investigation, using multipoint passive samplers, has revealed a good degree of uniformity of pollutants distribution across the region of study.

The air quality monitoring task has been completed. Field measurements relied on passive samplers and continuous monitoring equipment. For the measured compounds, it was found that they had very low concentrations compared to both industrial and residential KEPA standards, and accordingly

there is no violation of KEPA air quality standards. The measured pollutant concentrations reflect the meteorological conditions at the time of sampling. The only location (A20) downwind of the Az-Zour power plant did not show high concentrations of SO_2. It is expected that concentrations for some of the criteria air pollutants sampled, particularly for SO_2, could have been significantly higher had the meteorological conditions placed the passive samplers directly downwind of the Az-Zour power plant's flue gas.

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Characterization of BTEX sources in a medium-size city by concentration statistical analysis and GIS technique

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Abstract

The concentrations of benzene, toluene, ethylbenzene and the isomeric xylenes (BTEX) were determined in the atmosphere of S. Maria Capua Vetere city, in sixteen sites, ten times per site, during 2006. This city is of medium size, with about 32,000 inhabitants and is located in Southern Italy. Passive adsorption samplers, followed by GC/MS analyses, were used for BTEX determinations. The 24-hour average BTEX concentrations showed a marked variability from site to site. In some streets the pollutant concentrations were above the limit values required by the European Union. These streets were characterised by relatively intense traffic, but are rather narrow and have high buildings on either side. In the entire city the main pollutant source was road traffic. Moreover, analyses of the correlation coefficients among the BTEX concentrations and GIS maps highlighted the contribution of stationary sources to toluene air concentration. Their contribution has been quantified.
Keywords: BTEX, GIS technique, GC/MS analyses, pollutant concentration, diffusive sampler.

1 Introduction

Aromatic hydrocarbons, in particular benzene, toluene, ethylbenzene and xylenes (BTEX) are among the main pollutants in urban areas [1] and their adverse effects on human health are well documented [2]. Several studies [3, 4] have shown that the highest contribution to BTEX in urban areas is from the vehicular traffic. In many cases, however, it has been observed that emission from

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stationery sources, for example evaporation of solvents in factories and of fuel in fuel stations, also plays a relevant role [5]. Aromatic compounds emitted from the exhaust pipe consist mainly of unburned aromatic fuel components [6]. However, in the air the content of benzene, in relation to other aromatic compounds, is significantly higher than its fuel percentage, because benzene is a partially oxidized product of other aromatic compounds [7]. As these hydrocarbons react in the mesosphere with different rate constants, their relative concentrations change with the time of permanence in air [1].

This paper reports an investigation on BTEX concentrations in S. Maria Capua Vetere, carried out with the aim to analyse the relative impact on pollution levels of the road traffic and of small factories located in the urban area or in the suburbs. S. Maria Capua Vetere is a medium-size city, about 32,000 inhabitants, 0.6 cars per inhabitant, and is located in Southern Italy: lat. 41° 5' N, long. 14° 15' S.

2 Experimental

2.1 Sampling sites

The location of sampling sites is indicated in Figure 1. The sampling was performed on weekdays from February to November 2006 except August, 1 or 2 samplings per month. The data collected on rainy days were not included. All sampling points were located along the streets of the city, about 5 m above the ground level and not in proximity of cross-roads.

2.2 Analytical procedures

The BTEX compounds (benzene, toluene, ethylbenzene, o-xylene and (m+p)-xylene) were collected by Radiello® diffusive samplers, patented by Foundation *Salvatore Maugeri* (FSM). The exposition time for each monitoring campaign was 24 hours. The samplers consisted of a stainless steel net cylinder with a 100-mesh-grid opening, packed with 530 mg of activated charcoal. The analyses were carried on a Perkin Elmer GC-MS instrument, model Clarus 500 equipped with a thermal desorption instrument, model TurboMatrix ATD. A stream of helium of 80 mL min^{-1} at 320°C for 10 min was applied to the exposed cartridges to extract the analytes. These were condensed in a trap at 2°C. Then the trap was heated at 290°C for 1 min.

The column used was an Elite-5MS fused silica capillary, 30 m x 0.25 mm, 0.25 μm film thickness (Perkin Elmer Instruments). The oven temperature program was 35°C for 5 min, to 120° at 8°C/min and to 200°C at 15°C/min. The carrier gas was He at a flow rate of 1 ml min^{-1}. The mass spectrometer scanned from 35 to 300 a.m.u. every 0.1 s, in the electronic impact (70 eV) mode. The ion source temperature was 180°C and the multiplier voltage 350 V.

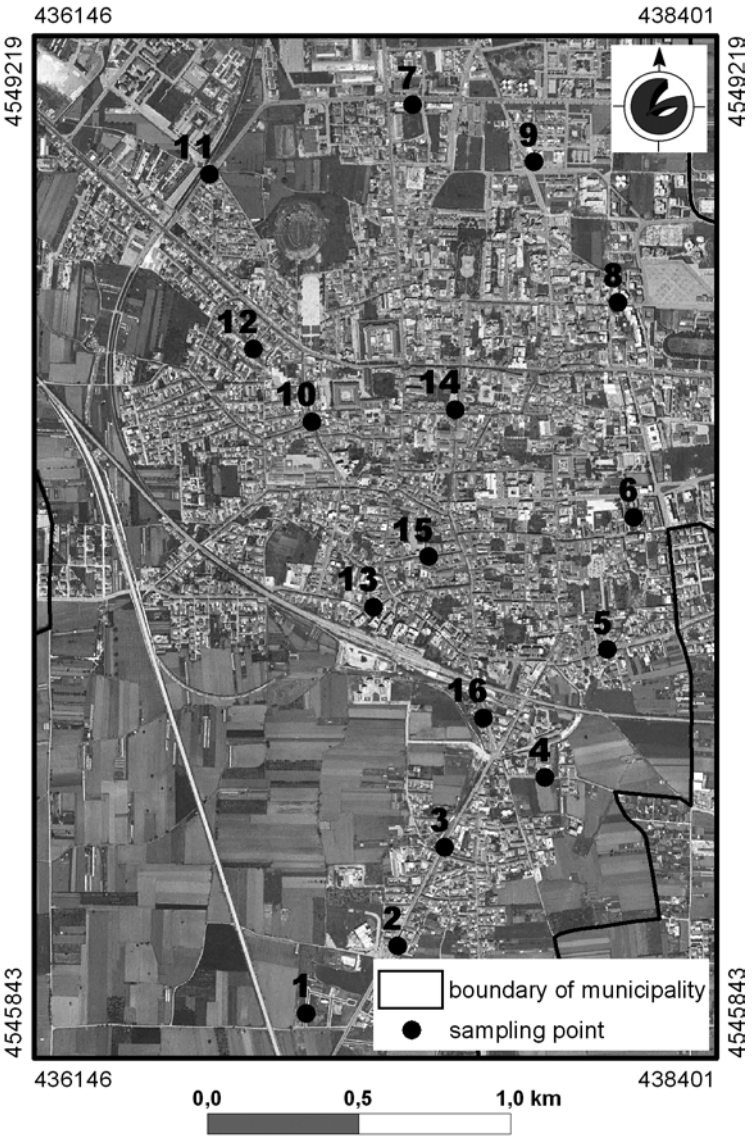

Figure 1: Map of the sampling points in S. Maria Capua Vetere.

2.3 Statistical analysis

Statistical analysis was carried out using the statistical software package Statistica 7 of StatSoft.

Table 1: Average BTEX concentrations (μg m^{-3}) recorded in 16 sampling sites in S. Maria Capua Vetere during 2006, 10 monitoring campaigns; standard deviations (%) in parenthesis.

site	benzene	toluene	ethylbenzene	(m+p)-xylene	o-xylene
1	3.8 (35)	12 (48)	2.3 (48)	5.4 (50)	2.6 (50)
2	4.7 (32)	15.7 (34)	3.1 (39)	8.3 (59)	3.8 (42)
3	7.5 (25)	29.5 (40)	6.6 (50)	18.5 (70)	8 (43)
4	5.9 (34)	15.5 (36)	3.5 (37)	9.3 (54)	4.5 (38)
5	11.4 (32)	34.6 (30)	7.6 (33)	21.2 (49)	10.3 (30)
6	4.0 (33)	12.6 (37)	2.6 (46)	6.5 (62)	3.2 (38)
7	5.3 (28)	21.0 (76)	3.5 (34)	9.0 (40)	4.6 (41)
8	5.1 (31)	14.3 (34)	3.2 (41)	8.8 (55)	4.2 (31)
9	4.3 (33)	29.8 (50)	3.2 (44)	8.4 (55)	3.7 (.35)
10	6.5 (25)	21.2 (37)	4.7 (34)	11.5 (33)	6.5 (40)
11	8.5 (21)	25.3 (23)	5.1 (43)	13.1 (64)	6.6 (55)
12	5.2 (60)	21.2 (67)	4.7 (70)	12.2 (80)	6.2 (49)
13	7.3 (30)	24.5 (43)	4.9 (49)	13.6 (74)	6.3 (49)
14	10.5 (22)	34.6 (23)	7.6 (26)	20.0 (35)	10.6 (30)
15	6.4 (33)	19.7 (47)	4.4 (48)	10.1 (40)	5.7 (51)
16	6.0 (2.4)	20.4 (10.5)	4.0 (2.0)	9.7 (5.2)	5.3 (3.0)
All the sites	6.5 (31)	22.4 (42)	4.0 (42)	9.7 (55)	5.3 (42)

3 Results and discussion

3.1 Concentrations in the sampling sites

Although this survey was carried out in a medium-size city, the average concentrations were relatively high in reference to the limit values required by the European Union. For example, we recorded an average value for benzene, computed using data from all the sites, of 6.5 μg m^{-3}, value higher than the limit value of 5 μg m^{-3} fixed by the EU. Table 1 summarizes the average BTEX concentrations recorded in S. Maria Capua Vetere during 2006. As can be seen, there is a marked difference from site to site, in spite of the relatively small size of the city: in the sites 5 and 14 we observed BTEX concentrations more than twice higher than the value observed in the site 1. This last site was in a street with low traffic intensity in a suburban area with no industrial activity in its immediate surroundings. Therefore, this sampling site was a good indicator of the background pollution level in the area. The higher pollutant concentrations were measured in sites 5 and 14. These were located in streets that had moderately intense traffic, but were relatively narrow and bordered by high buildings on either side. The canyon effect seems the dominant element in determining high pollution levels.

3.2 Statistical analysis

Statistical analyses by means of one-way ANOVA, followed by Tukey's test [8], of the 24-hour average concentrations recorded in each site showed that the differences among sites (discussed in the previous section) are statistically significant. For many couples of sites the P values were < 0.01. As regard the correlation among the BTEX concentrations, statistical analysis showed a strong positive correlation (Table 2).

Table 2: Correlation coefficients between 24-hour average BTEX concentrations recorded during 2006 in the city of S. Maria Capua Vetere.

	Benzene	Toluene	Ethylbenzene	(m+p)-Xylene	o-Xylene
Benzene	1	0.76	0.90	0.83	0.88
Toluene		1	0.81	0.71	0.77
Ethylbenzene			1	0.91	0.97
(m+p)-Xylene				1	0.83
o-Xylene					1

This suggests that in the city there is one major source of BTEX, probably the vehicular traffic. However, the correlation coefficients obtained in the present study are lower than the coefficients reported by us [9] and those for similar works [10, 11]. It is interesting to note that the lowest coefficients were observed

for toluene versus all the other pollutants. Comparison of correlation matrixes, computed excluding in turn the contribute of each site, showed that the sites 7, 9 and 11, all located in the north of the city (Figure 1), contributed markedly to lower the correlation coefficients. When these were excluded from the analysis, a marked increment of the coefficient values was observed. Table 3 reports the correlation matrix computed without the contribution of these sites.

Table 3: Correlation coefficients between the 24-hour average BTEX concentrations calculated without the data recorded in sampling sites 7, 9 and 11.

	Benzene	Toluene	Ethylbenzene	(m+p)-Xylene	o-Xylene
Benzene	1	0.90	0.91	0.84	0.90
Toluene		1	0.92	0.82	0.90
Ethylbenzene			1	0.91	0.97
(m+p)-Xylene				1	0.84
o-Xylene					1

Coherently with this result, a coefficient matrix computed using only the data from the sites 7, 9 and 11 has low coefficients, particularly for the toluene terms (Table 4). This result is a clear indication of toluene emission not only from vehicular traffic but also from stationary source at the sites 7, 9 and 11. Assuming that the ratio between toluene and benzene concentrations in the other sites reflects emission from traffic we computed that about the 40% of toluene in the atmosphere at sites 7, 9 and 11 was from the stationary source.

Table 4: Correlation coefficients between the 24-hours average BTEX concentration calculated using only the data recorded in the sampling sites 7, 9 and 11.

	Benzene	Toluene	Ethylbenzene	(m+p)-Xylene	o-Xylene
Benzene	1	0.27	0.81	0.73	0.74
Toluene		1	0.46	0.37	0.36
Ethylbenzene			1	0.90	0.95
(m+p)-Xylene				1	0.82
o-Xylene					1

Figure 2 shows the concentration gradient maps for benzene and toluene as obtained by GIS software. In agreement with the results of the coefficient matrix, there are significant differences between the two maps. In the top of the benzene map we observe lower concentration, while in the toluene map we observe a relative maximum.

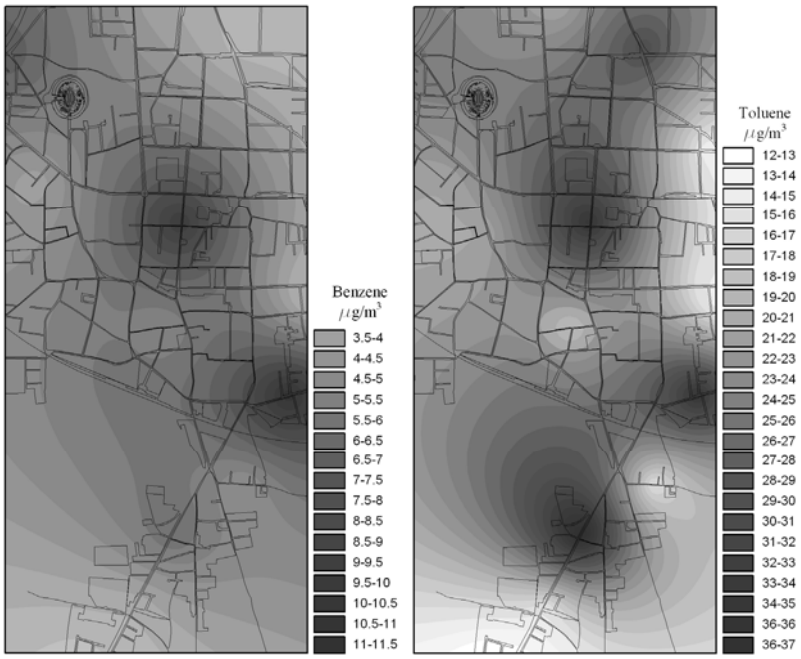

Figure 2: Benzene (left) and toluene (right) concentration distributions in S. Maria Capua Vetere, as obtained by GIS software.

4 Conclusion

The results presented here show that air pollution analysis by passive samplers distributed in the studied area combined with appropriate statistical treatment and GIS elaboration of the data, is a powerful technique for environmental control. Not only it provides detailed information on the pollution levels throughout the territory, but also permits to identify minor stationary sources.

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Potentialities of Vis-NIR spectroradiometry for mapping traffic emissions in urban environments

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Abstract

Traffic emissions introduce in urban environments low-reflectance matter, which affects the optical properties of atmosphere and consequently of soils, where particulate matter is accumulated. Radiometric techniques, focused on the 350-2500 nm wavelength range, were applied to investigate the alteration of optical properties of soils in urban environments. An integration between radiometric data and geochemical analyses was made to estimate the relationship occurring between optical properties of soils and their heavy metals content, which may trace traffic pollution. Soil samples were sampled in two study areas and treated to perform geochemical analyses and spectroradiometric acquisitions. An experimental analytical protocol was developed to study the optical properties of soils. The optical properties of urban soils are influenced by the deposition of carbonaceous particles and by the interaction between soil phases and traffic emissions. Results showed that the integrated approach of radiometric and geochemical investigations is a valid tool for monitoring traffic emissions in urban environments.
Keywords: soil geochemistry, spectral analysis, urban pollution, radiometry.

1 Introduction

Monitoring of pollution in urban environments is one of the major challenges for the scientific community. The urban environment is a complex, heterogeneous system, being characterized by different climatic, urban and geological features. The investigation of each of these characteristics can be performed by a great

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variety of techniques and methods. Although these tools are nowadays very advanced and allow scientists to thoroughly investigate each task, a complete survey about the anthropic impact on the urban system requires a considerable amount of time and resources.

Soils are exposed towards contaminants and can record the atmospheric pollution. The pedosphere is conventionally investigated using geochemical techniques (Fergusson [5]), even though these methods are expensive and time consuming. Geochemical analyses are usually performed on major elements (i.e. Fe, Al, Mn), which are mainly associated with the mineral phases, and to heavy metals (Pb, Ba, Zn, Cu and Cd), that are a primary constituent of most vehicular parts and fuels (Hamilton and Harrison [7]). These metals are already present in the soil parent material and can migrate through the soil profile as a result of pedogenesis. The anthropic fallout can be fixed by soils, adsorbed by organic matter, clay minerals and iron-manganese oxy-hydroxide.

Reflective spectroscopy, which is based on the interaction between electromagnetic radiation and matter, is possibly an alternative method to contribute the monitoring of soil pollution. This discipline is a branch of radiometry and studies light, as a function of wavelength, which has been reflected or dispersed by a solid, a liquid or a gas. When photons intercept a solid surface, some of them are reflected, some are transmitted and others are absorbed. The reflected scattered photons strike other grains and are dispersed far away from the surface to be detected and measured. Minerals, due to several processes, absorb photons. The variety of absorption phenomena and their relationship with specific wavelength provides information about the mineral chemistry (Leone and Sommer [8]; Palacios-Orueta and Ustin [9]) and different soil properties (Galvao et al. [6]; Undelhoven et al. [11]). In this context several studies are focused on the detection of the relationship between reflectance and chemical parameters. This technique was tested mainly in large rural areas, where mineralogical and pedological properties are strongly different. Most of these applications are, in fact, dedicated to agricultural purposes and to the land management. These objectives are not accomplishable in an urban context, because soil differences are more subtle, thus making soil identification more difficult. The hypothesis which support the using of reflective spectroscopy in urban environments is that anthropic emissions introduce dark particulate matter which, falling out on the ground and interacting with soils, can alter optical properties of soils.

2 Study area

Rome is an ideal site to investigate soil contamination. It is the sixth largest European city (City Majors [2]) with about 2,700,000 residents widespread over 360 km^2 wide district; about 50% of this area is heavily urbanized. In this region and in the surrounding area, large industrial or thermo-electric plants are absent; thus the major source of atmospheric pollution is vehicular traffic, estimated to exceed more than 2,000,000 vehicles, circulating daily all over the urban road pattern.

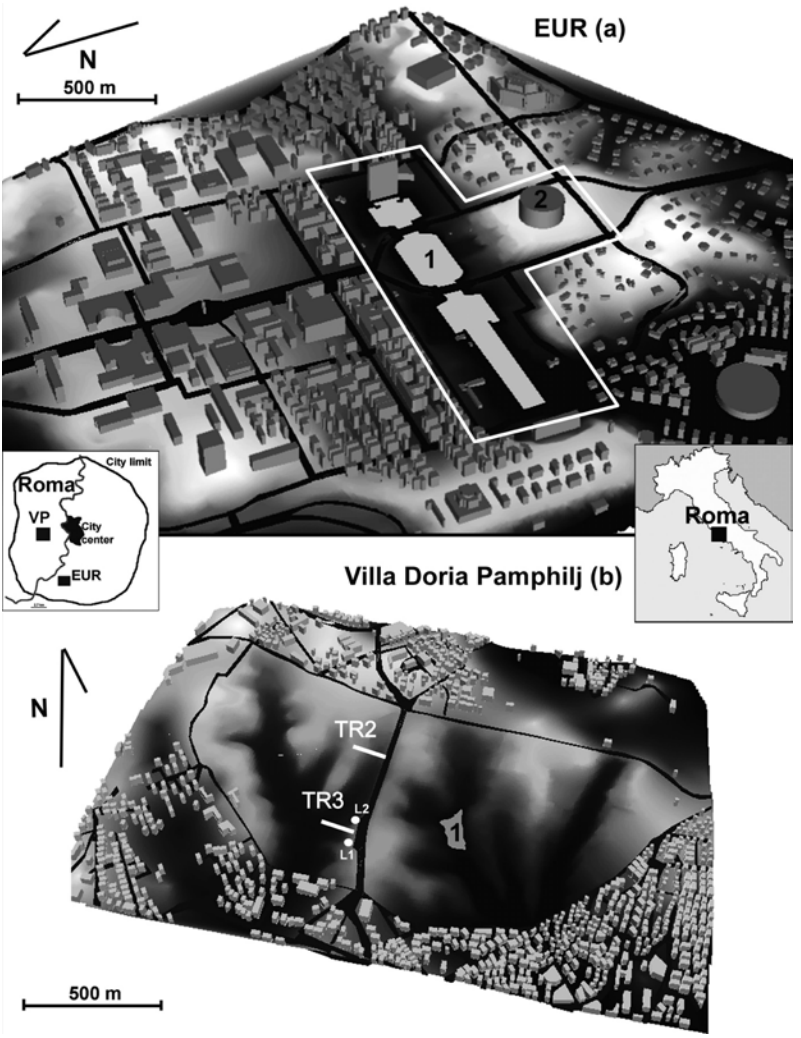

Figure 1: Location of the study areas: the EUR District (a) and Villa Doria Pamphilj (b). Lakes (1) and the Sport Center (2) are positioned in the map. In white the sampled sites.

A "test" site and a "check" site were selected in the city of Rome. The former is the EUR District, which is one of the most polluted areas of the city (Comune di Roma [4]) and it has a dense road pattern (Figure 1). In particular the test site is a relatively large green area, measuring 4 km^2, which surrounds an artificial lake (EUR lake), built in 1960. When the road adjacent to this site was built, soils were completely reworked. About 100.000 vehicles pass daily along this

road. The "check" site, Villa Doria Pamphilj, is a park, created in the 18th century, and it is 2.5 km^2 wide and 4 km far from the city centre. The integrity of this green area was interrupted in 1960, when a big road was built: this road cuts the park in two parts and it is travelled by more than 70,000 cars/day. This second area allowed checking the results obtained in the "test" site. In both test sites, soils are composed of filling materials resulting from the reworking of volcanic rock, belonging to an eruptive volcanic sequence (Salzano [10]).

3 Sampling

In both study areas, each sample was composed of three parts collected with a probe, 10 cm deep in the ground.

In the EUR district, a stratified sampling strategy was carried out and 118 soil samples were collected (Figure 1(a)): the main grid was made of cells of 40 x 40 m, properly oriented to include the entire study area. Sampling sites were randomly selected in a 10 x 10 m cells lattice.

Two soil transects were sampled in Villa Doria Pamphilj (Figure 1(b)). Assuming Villa Doria Pamphilj as a single-source site, an oriented sampling strategy was created. Transects, orthogonal to the main road, were sampled in correspondence of different operating conditions of vehicles and were sampled up (25 samples) to the distance of 100 m far from the main road. One is located were cars are accelerated (TR2) and one where vehicles are queued (TR3).

4 Methods

All the samples were sieved to obtain soil particles less than 1 mm and dried out at 105°C.

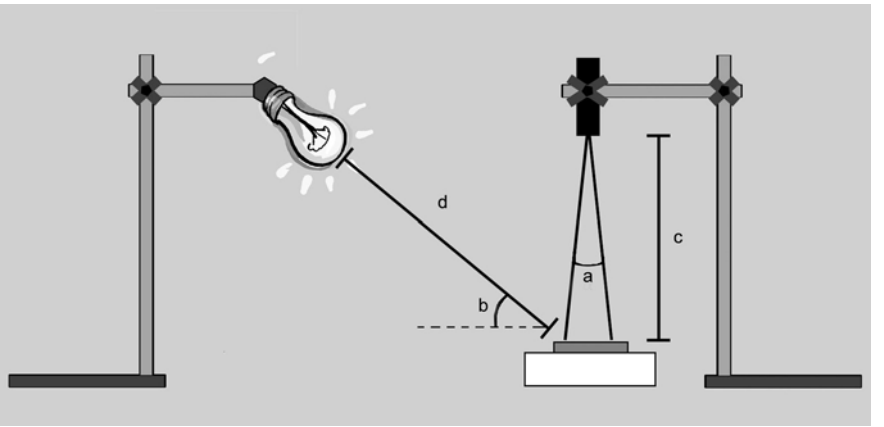

Figure 2: Experimental set up of laboratory reflectance measurements. Notes: (a) Sensor field of view; (b) Light angle of incidence; (c) Optic sensor distance; (d) Light source distance.

4.1 Elemental analysis

Soil sample solutions were prepared by HF-$HClO_4$ hot digestion. For elemental analysis of Ca, Al, Fe, Ba, Zn and Cu a Perkin-Elmer ICP-OES Optima 2000 was employed. Pb and Cd were determined by HGA-AAS, Perkin-Elmer 5100.

4.2 Radiometry

Reflectance data were acquired by a field-portable Spectroradiometer (Fieldspec) that measures the reflected solar radiation energy in the wavelength range 350-2500 nm.

The experiment set up is shown in Figure 2. All the analyses were performed in a dark room. Heterogeneities of the sample surface were taken into account by measuring differences obtained varying the position and the orientation of the material. Each sample was measured in 12 different positions and the instrumental error was estimated to be smaller than 3%.

4.3 Geostatistics

Distribution maps of each investigated element were obtained applying geostatistical criteria (Armstrong [1]) to the sampled soil dataset. It was necessary to apply a deterministic interpolation method for all the analysed chemical elements because of the complex shape of the study area.

5 Radiometry

The experimental dataset, containing all the spectra acquired in sampled soils, shows two major variations. The morphometric study of soil spectra was performed by taking into account three main features: the colour index, calculated as a reflectance integrated between 490 and 700 nm; the slope angle of the spectral curve between 500 and 800 nm; the spectral height, calculated as the mean value of reflectance values between 1520 and 1720 nm. Effects due to grain size are significant in presence of large grain size variations. Sampled soils showed minor variations of the grain size composition. The presence of clays is small and does not justify the changes observed in radiometric spectra.

5.1 EUR district

Distribution maps of these indexes were compiled (Figure 3). The soil colour has a “spotted” distribution characterized by the absence of specific trends. The soil spectra height and possibly the signature slope show a distribution affected by their distance from the road. The centre of anomalies observed on these maps are, especially in the case of spectrum height, coherent with those concerning Pb. Lead maps, used as a traffic tracer, can help to compare the radiometric results with the plausible vehicular circulation model.

Results show that areas with lower spectral height indexes and spectral slope indexes are coherent with anomalous lead regions. It is clear how polluted areas can be outlined with this method and how soil radiometric spectra change in correspondence to traffic pollutant sources. More investigations and a larger

statistical sample are needed to associate these anomalies with a specific chemical contamination.

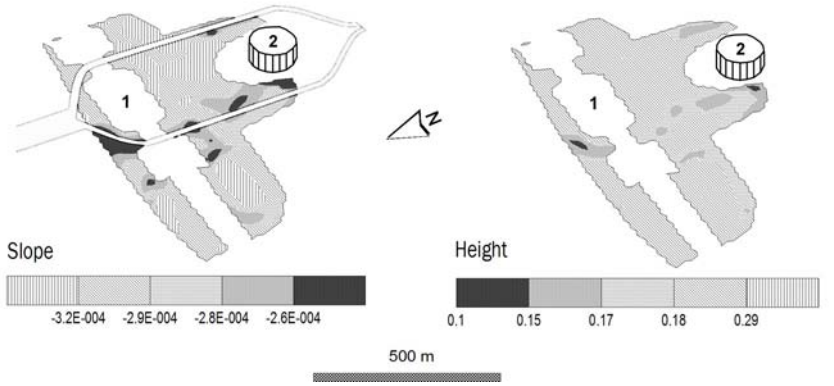

Figure 3: Maps of the distribution of soil spectroradiometric indexes. Eur Lake (1), Sport center (2) and main road are shown.

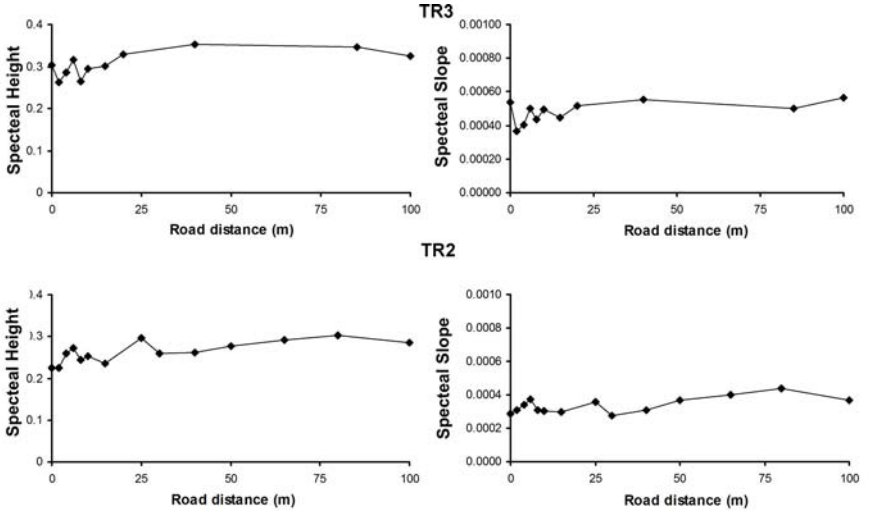

Figure 4: Distribution of spectroradiometric indexes in the soil transects.

5.2 Villa Doria Pamphilj

Reflectance values showed high affinities with the Pb content in most of the investigated interval of wavelength. The proportionality is, also in this case, inverse but it is controlled above all by the road distance. The geometric indexes previously described evidence perfectly this spatial dependence (Figure 4). Radiometric indexes (slope and height) are lower close to the main road and they

reach the highest values at a distance of more than 30 m from the road. Trends are evident if we consider that anomalous values are located close to trees and manufacts, that reduce the exposure of soils towards the atmospheric fallout. The comparison between the two soil transects shows that TR2 has lower values of the calculated indexes than TR3.

6 Soil geochemistry

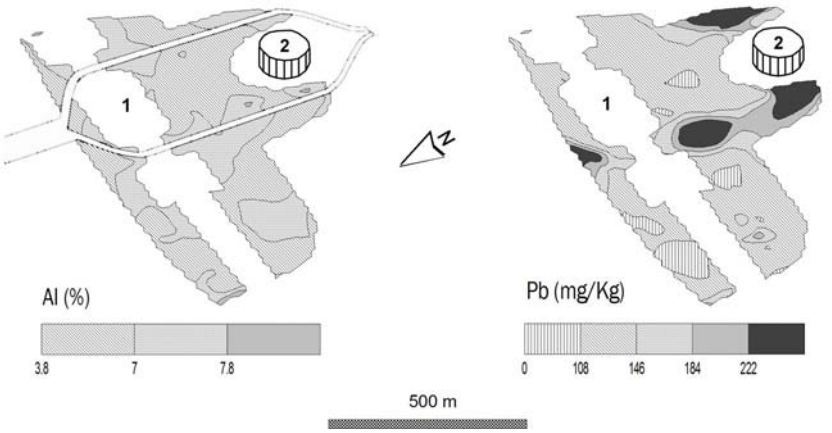

Figure 5: Maps of the distribution of Al and Pb as derived from geochemical analysis. Locations of Eur Lake (1), Sport center (2) and of the main road are shown.

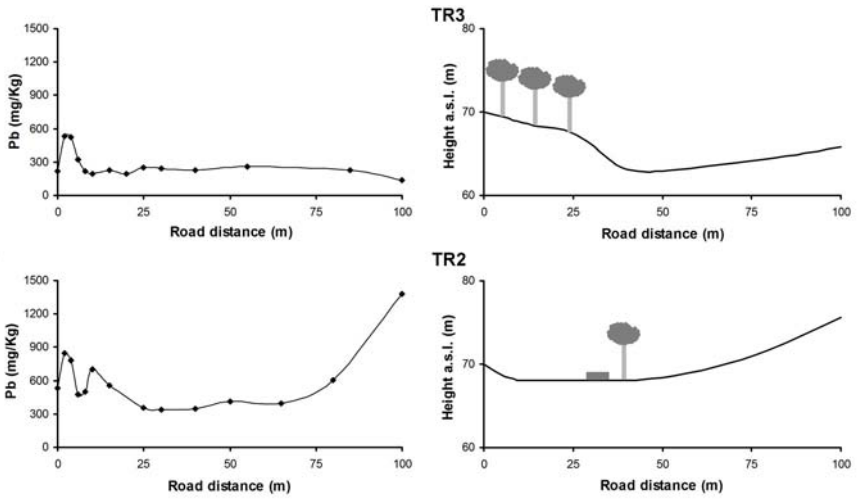

Figure 6: Soil transects TR2 and TR3. The Pb content is on the left while the topography and the presence of vegetation and manufact are on the right.

6.1 EUR district

Table 3 summarizes the chemical analyses performed on soils sampled in this test area. Major elements (Al, Fe, Ca and Mn) show small variations compared to minor metals (Ba, Zn, Cu, Pb and Cd). An example of the maps concerning the spatial distribution of the chemical elements is shown in Figure 5. The combination of several features (i.e. mineralogy, pedology, vegetation, geology) controls the variation of soil composition and consequently the distribution of each element. Major elements (Al, Fe, Mn and Ca) and some heavy metals (Ba, Zn, Cu and Cd) showed a distribution with values close to the mean within the entire sampled area. Small anomalous areas occur in "confined area". It is reasonable to assume that the high natural concentration of these elements in soils, due to the volcanic nature of the bedrock, makes it difficult to discriminate the concentration related to urban pollution from that of soil natural background. The local anomalies can be explained by the heterogeneity of the soil in the study area, due to the quantity of fills present.

Pb distribution differs from that of other elements, as it is influenced by the road network. Strong anomalies are located in correspondence of the two carriageways. The highest lead content in soils, that exceeds two or three times the natural background value (about 100 mg/Kg), was found close to traffic lights and where a change in road slope occurs. Moreover the anomalous content areas are confined to a strip that is one hundred meters far from the main roads.

6.2 Villa Doria Pamphilj

In this confirmation site only lead was analysed, as in the previous case we demonstrated that this element is clearly affected by anthropic emissions and is a good tracer of vehicular emissions. Soil transects TR2 and TR3 differ from each other for their topography and for the presence of vegetation (Figure 6). Traffic conditions represent an additional feature: vehicles moving in proximity of TR2 generally speed up, while reaching the area where TR3 occurs, they slow down. The lead content along the transects generally decreases with increasing distance from the road, except the higher values along transect TR2 (around 1000 mg/kg, found in samples located further from the road, at a distance of 80 and 100 m). This anomaly is located on the hill positioned in front of the road and it can be explained as the result of wind blowing that carries the traffic plumes towards the hill. All the discrepancies, showed in the decreasing trend of lead versus the distance from the main road, are located in correspondence of trees, bushes and manufacts, that reduce soil exposure towards atmospheric fallout.

7 Discussion

Soil chemistry defines a condition of urban pollution, where Pb shows significant contamination levels influenced by road pattern. Investigated sites represent two different urban conditions: EUR district has a green area included in a traffic-dense area; Villa Doria Pamphilj is a green area, relatively uncontaminated, which contains and isolates a high-traffic road.

EUR district permitted investigating the contamination of urban soils in a dense urbanized area, where different roads are present. Maps built using radiometric features (Figures 5 and 6) show a distribution similar to those obtained by a "traditional" geochemical approach (Figures 3 and 4). The spectrum features identify anomalies on the main roads, which can be justified considering traffic in this area, uphill in the western carriageway and downhill in the eastern one (Figure 1(a)). When cars are queued or hold up and do not accelerate, gas pressure is low and particles remain in the exhaust tube, nucleating and growing. When cars accelerate, they emit these dust grains because of the high gas pressure. Driving uphill on the western main carriageway, the exhaust pressure is higher and constant with respect to the opposite sense of direction, where cars travel downhill. The lower spectrum heights and the highest spectrum slope values are located obviously at traffic lights where cars speed up or accelerate to cross the slope. The spectral height and slope maps (Figure 10) differ, probably due to the interference occurring between natural soil heterogeneities and traffic dust fallout (i.e. wind direction, dust content, particulate granulometry).

Villa Doria Pamphilj permitted investigating soils contaminated by a single source and to better comprehend the interaction between soils and radiometry. Coherent conclusions can be carried out with soil transects, which show a decreasing trend of the lead content and increasing trend of spectral indexes with distance from the main road. Some anomalies from these trends were observed and they can be explained noting that index values above the trend are located where vegetation and manufacts are present. This observation is coherent with those evinced from lead trends, that show lower Pb content in the same locations. Vegetation and manufacts, therefore, mitigate the soil exposure towards atmospheric pollutants and prevent the contamination of soils. The comparison between the two transects confirms that the soil contamination depends on circulating conditions of vehicles. TR2 is located where vehicles are launched at high velocity, while TR3 is positioned where cars are decelerating close to a traffic light.

The "spectral height index" and the "spectral slope index" are features directly relatable to the presence of carbonaceous and/or metallic particles. Low and constant reflectance values, across all the wavelength range, characterize, in fact, spectra of metallic oxides and black carbon (Clark et al. [3]). This atmospheric deposition may also alter the optical properties of soils or may induce a degradation of soil constituents.

Further studies are of course needed for improving the knowledge about the spectroradiometric signature of traffic fallout and about properties changing of soils in response to bad quality of air.

8 Conclusions

The geochemical investigation allowed identification of highly polluted soils and to estimate their dependence on vehicular operating conditions. The comparison between radiometric results and geochemical analyses performed on urban soils

showed that the resulting distribution maps are coherent and influenced by the vehicle operating conditions. Radiometric variations of spectra suggest that the content of traffic dust in urban soils affects the radiometric signature of these materials. As urban particulate matter is composed mainly of black grains, polluted soils tend to adsorb more light than less traffic-exposed soils. These results demonstrate that radiometry has good potentialities for monitoring urban pollution in combination of geochemical analyses.

In conclusion, radiometry allow investigation of urban areas with a detailed spatial resolution at a relatively low cost. The geochemical characterization of anomalous areas is the second step of this approach and it is necessary to quantify soil pollution.

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A pilot investigation into the potential of mineral magnetic measurements as a proxy for urban roadside particulate pollution

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Abstract

The use of mineral magnetic concentration parameters (χ_{LF}, χ_{ARM} and SIRM) as a potential particle size proxy for urban street dust collected from Southport (Merseyside, UK) is explored. Correlation analyses between each magnetic parameter and traditional particle size classes (i.e. sand, silt and clay) and respiratory health related size classes (i.e. PM_{10}, $PM_{2.5}$ and $PM_{1.0}$) are reported. Significant relationships ($p < 0.001$; $n = 50$) exist between sand, silt and clay content with at least one or all of the magnetic concentration parameters. This is also the same for each PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ sizes. Of the three magnetic parameters, χ_{LF} displays the strongest correlation values ($r = 0.701$, $P < 0.001$, $n = 50$) and is the most significant parameter, which is consistent with all class sizes of each approach. In doing so, these associations indicate mineral magnetic measurements have considerable potential as a particle size proxy for determining urban roadside particulate matter concentrations. Given the speed, low-cost and sensitivity of the measurements, this suggests magnetic techniques could potentially be used as an alternative and/or complementary exploratory technology for pilot particulate pollution investigations. Furthermore, in certain instances, it could be useful for examining linkages between respiratory health and particulate pollution and vehicle emissions.

Keywords: environmental magnetism, particle size, urban street dust, built environment, epidemiology, public health.

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1 Introduction

Urban pollution, particularly particulate matter (PM), continues to be intensively studied because dust particles can exert a potentially harmful influence on public health, especially those susceptible to respiratory illness [1, 2]. It is customary to analyse particulates of two size fractions; the coarse fraction PM_{10} ($d_a \leq 10$ μm) and fine fraction $PM_{2.5}$ ($d_a \leq 2.5$ μm). More recently, the adopted changeover point between coarse and fine particles occurs at $PM_{1.0}$ ($d_a \leq 1.0$ μm). The success or failure of the respiratory defence systems partly depends upon the size of the particulates inhaled and the depth of their penetration into the respiratory tract. A recent assessment by the 'Expert Panel on Air Quality Standards' [3] concluded that both coarse and fine fractions represent health risks, although the disease outcomes may differ for the two size fractions [4].

Since 1997, UK local authorities have been reviewing and assessing air quality in their area, to work towards meeting the national air quality objectives. There are over 1500 monitoring sites across the UK, which monitor air quality (monitoring PM_{10} concentrations, amongst those of several other pollutant measurements). In 2003 the UK Government set lower limits for fine particle concentrations, which need to be reached by 2010. Currently, the main source of airborne fine particulates in the UK is road traffic emissions. However, it is estimated, by 2010, that road transport emissions of fine particles will fall by two-thirds of those a decade ago [5]. Moreover, the European Commission has proposed that the legislation on particulate matter should be supplemented by setting a limit value of 35 $\mu g/m^3$ for $PM_{2.5}$ particles and an interim reduction target of 20% to be attained between 2010 and 2020 [6]. Assessment of the extent and severity of urban dust concentrations requires thorough investigation before Air Quality Management Plans and remediation can be instigated, which means that there is scope for new PM monitoring technologies.

It is, therefore, timely for innovative PM technologies to be considered as an alternative, or in tandem, to those already employed to determine $PM_{2.5}$ and PM_{10} concentrations. Moreover, ideally, they need to be rapid, reliable and inexpensive. However, to assess the suitability of any analytical technique as an efficient particle size proxy it is necessary that the nature of the relationship between the proposed parameters and particle size follow a predictable pattern. Many studies have previously explored relationships between mineral magnetic measurements and the physico-chemical properties of soils, sediments and dusts. Based on these investigations, from a host of environmental settings (e.g. soils, deserts, glacial, lakes, coastal and marine), magnetic measurements have previously been identified as a suitable proxy for geochemical, radioactivity, organic matter content and particle size data.

Two hypotheses are tested here. Firstly, the extent to which particular magnetic concentration parameters can be used as a particle size proxy for urban street dust and, secondly, whether theses data associations follow the predictable trends of other environmental studies [7–9].

2 Case study

The town of Southport (2216 hectares), part of Sefton Metropolitan Borough Council (Merseyside, UK), located between the cities of Liverpool and Preston, is a coastal resort in NW England (Figure 1). Founded in 1798, visitors have been coming to Southport's stunning expanse of sandy beaches (~35 km long) and seaside attractions for over two centuries and these are still immensely important to the town today. However, much of the town's major growth was in the 19th Century, when it gained a reputation for being a refined seaside resort, and this is still reflected in much of the town's design

The town centre has wide streets, lined with shops, banks and civic buildings (Lord Street, Chapel Street, Eastbank Street, London Street), which include a tree-lined boulevard (~2 km long) decorated with imposing three and four storey Victorian (1837-1901) buildings. Nowadays, these ornate buildings, fronted with glass awnings, serve as exclusive shopping outlets. Lord Street is where the town started, from a valley in the sand dunes, and it is this that defined the geography of early Southport and its road network [10].

Surrounding the town centre is a suburb of Victorian and Edwardian detached and semi-detached houses, which, further away, become progressively grander (with turrets and chateau-like towers) until reaching the modern housing estates clustering the town's limits. Together, these are home to a population of 91,404 (2001 Census) [11].

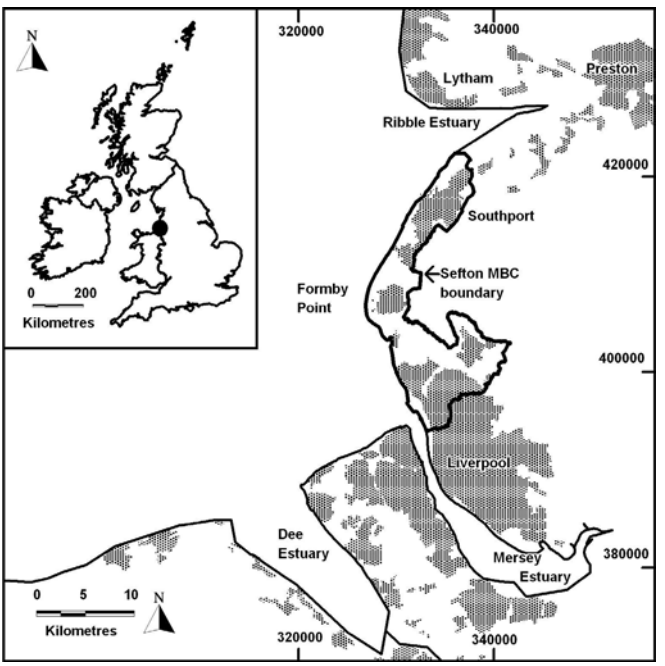

Figure 1: Location map of Southport and its position within Sefton MBC.

2.1 The context for focussing on Southport town centre

The strategy for Transportation in Southport (TRANSIS 2010) was published in 1999 and, subsequently, in 2000, incorporated into the Merseyside Local Transport Plan (Merseyside LTP). The Merseyside LTP identified a 10-year transportation strategy for Merseyside, with a five-year programme of investment focused on strategy delivery. The aim is to develop a fully integrated and sustainable transport network for Merseyside, which supports economic, social and environmental regeneration and ensures good access for all the community. The Merseyside LTP transport investment programme in Sefton includes a variety of schemes and initiatives. Sefton has benefited from over £35.4m (provided by central Government) of investment in transport schemes, namely the construction of the Marine Way Bridge (£7.7m); improvements to Nevill Street (£1.5m); improvements to Eastbank Street (£0.85m); and the pedestrianization of Chapel Street (£4m) (Figure 2), amongst other work within the Borough [12].

Figure 2: Chapel Street (a) prior to redevelopment (May 2005) and (b) close to finishing the redevelopment (January 2007).

The TRANSIS 2010 strategy aims to support and contribute to Southport's continuing success in retail, tourism, leisure and business. This means retaining good access to the town, easing circulation within the town and enhancing the environment, both in the town centre and surrounding residential areas. The strategy is based around three key themes: economic regeneration; increased access and mobility and environmental improvement [12].

2.2 Pedestrianization of Chapel Street

Chapel Street is one of the main shopping areas in Southport and is also the main arrival point for visitors travelling by public transport. As such, Chapel Street is being converted from a street dominated by busy traffic to create a safe, attractive and fully pedestrianized area for shoppers and visitors, with trees, seating, improved street-lighting, CCTV security cameras and ample space. The Chapel Street scheme is viewed as an essential element in the regeneration

of Southport and in raising the profile of the town as a vibrant and successful commercial, retail and leisure destination and being a 'Classic Resort' [12].

The closure of Chapel Street will result in traffic being transferred onto other routes in and around the town centre. Therefore, specialist consultants were employed to conduct an impact assessment of this on the town centre. This showed that projected traffic displaced as a result of the pedestrianization could be accommodated within the existing town centre highway network [12].

3 Materials and methods

Samples used in this study form the first stage of an on-going investigation by the authors. Prior to redevelopment work starting, street dust samples were collected from all town centre roads and the sites georeferenced (May 2005). The redevelopments are now scheduled to finish early 2007. After which (May 2008), it is proposed that the same sites will be re-sampled. Subsequently, spatial variations in the magneto-chemical properties of the particulate pollution will be compared with those of the first stage, so as to identify how changes in traffic direction and flow relate to any changes in spatial particulate pollution patterns.

3.1 Sample collection and preparation

Street dust was collected from the pavements (sidewalks) of town centre roads. Typically, 10–50 g dust samples were collected (from ~1 m^2) by brushing with a small hand-held fine-bristle brush. Dust was then transferred to clean, pre-labelled, self-seal, airtight plastic bags. In the laboratory, samples were visibly screened to remove macroscopic traces of hair, animal and plant matter.

3.2 Mineral magnetic measurements

All samples were subjected to the same preparation and analysis procedure. Samples were dried at room temperature (<40°C), weighed, packed into 10 ml plastic pots and immobilized with clean sponge foam and tape prior to analysis. Initial, low-field, mass-specific, magnetic susceptibility (χ) was measured using a Bartington (Oxford, England) MS2 susceptibility meter. By using a MS2B sensor, low frequency susceptibility was measured (χ_{LF}). Anhysteretic Remanence Magnetisation (ARM) was induced with a peak alternating field of 100 mT and small steady biasing field of 0.04 mT using a Molspin (Newcastle-upon-Tyne, England) A.F. demagnetiser. The resultant remanence created within the samples was measured using a Molspin 1A magnetometer and the values converted to give the mass specific susceptibility of ARM (χ_{ARM}). The samples were then demagnetized to remove the induced ARM and exposed to a series of successively larger field sizes up to a maximum 'saturation' field of 1000 mT, followed by a series of successively larger fields in the opposite direction (backfields), generated by two Molspin pulse magnetisers (0-100 and 0-1000 mT). After each 'forward' and 'reverse' field, sample isothermal remanent magnetisation (IRM) was measured using the magnetometer.

3.3 Laser diffraction measurements

All samples were subjected to the same textural preparation and analysis procedure, using sieving (2000 μm aperture) followed by laser diffraction analysis. Low Angle Laser Light Scattering (LALLS), using a Malvern (Malvern, England) Mastersizer Long-bed X with a MSX17 sample presentation unit, enabled rapid measurement of particle sizes within the 0.1–2000 μm range. Macroscopic traces of organic matter were removed from representative sub-samples before being dampened by the dropwise addition of a standard chemical solution (40 g/l solution of sodium hexametaphosphate ($(NaPO_3)_6$) in distilled water) to help disperse aggregates. To ensure complete disaggregation, each slurry was then subjected to ultrasonic dispersion in a Malvern MSX17 sample presentation unit. For greater precision, the mean of five replicate analyses was measured with a mixed refractive indices presentation setting. A standard range of textural parameters was calculated, including the percentage of sand, silt and clay class sizes and their sub-intervals. The Malvern instrumentation was regularly calibrated using latex beads of known size.

4 Results

Particle size data (n = 50) indicates samples are dominated by sand (~65%), silt (~32%) and clay (~2%), in respective orders (Table 1). Given the coastal setting of the town and visual inspection of quartz-dominant grains in the samples, it is presumed that most sand-size material is wind-blown and derived from the local foreshore.

Table 1: Summary particle size properties of urban roadside particulates (a) traditional sediment size fractions and (b) respiratory health-related size fractions (n = 50 samples).

	Mean (%)	Maximum (%)	Minimum (%)	Standard Deviation
Sand (63–2000 μm)	65.14	75.62	42.11	5.34
Silt (2–63 μm)	32.73	53.77	22.57	4.94
Clay (<2 μm)	2.13	4.12	1.39	0.49

	Mean (%)	Maximum (%)	Minimum (%)	Standard Deviation
$<PM_{10}$	9.10	15.56	6.33	1.81
$<PM_{2.5}$	2.64	4.90	1.77	0.57
$<PM_{1.0}$	0.85	2.44	0.51	0.33

From a respiratory-health perspective, PM_{10} grains represent ~9%, $PM_{2.5}$ ~3% and $PM_{1.0}$ ~1% of the dusts at pavement level. Since the town has no heavy

industrial activity, it is presumed that the most local anthropogenic PM pollution is derived from vehicle emissions. However, this is probably not exclusive because, depending on wind direction, some PM pollution may be derived from the regional cities of Liverpool and/or Preston.

Once suspended, particles <10 μm in diameter are able to remain airborne for hours or days and, in some cases, even weeks (Harrison, 2004). Therefore, the presence of PM of these sizes on pavement surfaces indicates either the dusts have not been disturbed recently or they have only just settled-out. That said, since the town centre pavements normally receive frequent and heavy foot-traffic, it is assumed the time of sampling (0500 – 0800) and the weather conditions (warm, dry and still) have permitted sizeable PM accumulations.

Table 2 summarizes the mineral magnetic characteristics. χ_{LF} is roughly proportional to the concentration of ferrimagnetic minerals within the sample, although in materials with little or no ferrimagnetic component and a relatively large antiferromagnetic component, the latter may dominate the signal. χ_{ARM} is particularly sensitive to the concentration of magnetic grains of stable single domain size, e.g. ~0.03–0.06 μm. SIRM is related to concentrations of all remanence-carrying minerals in the sample, but is also dependent upon the assemblage of mineral types and their magnetic grain size. These data indicate the samples contain moderate to high magnetic concentrations. Yet, compared with previous urban magneto-dust studies, the mean values are similar to those of Liverpool (23.7×10^{-7} m^3 kg^{-1}) [13] and Shanghai (29.9×10^{-7} m^3 kg^{-1}) [14].

Table 2: Summary mineral magnetic properties of urban roadside particulates (n = 50 samples).

	Units	Mean	Maximum	Minimum	Standard Deviation
χ_{LF}	10^{-7} m^3 kg^{-1}	27.95	62.80	14.33	9.91
χ_{ARM}	10^{-7} m^3 kg^{-1}	0.30	0.65	0.00	0.17
SIRM	10^{-5} Am^2 kg^{-1}	2345.41	6291.61	1189.11	946.26

Table 3 shows the Pearson's correlation coefficient values (r) between the mineral magnetic concentration parameters and particle size parameters, grouped according to traditional sediment size fractions and respiratory health-related size fractions. Significant relationships ($P < 0.001$; $n = 50$) exist between sand, silt and clay content with at least one or all of the magnetic concentration parameters. This is also the same for each PM_{10}, $PM_{2.5}$ and $PM_{1.0}$ sizes. However, of the three magnetic parameters, χ_{LF} has the strongest and most significant correlation values and, furthermore, is consistently significant ($P < 0.001$) with all class sizes from both groups. χ_{ARM} has mixed significance levels ($P < 0.01$ and $P < 0.05$) for both groups, yet has no association with PM_{10}. In contrast with both these parameters, SIRM only has significant ($P < 0.05$) kinships with the very finest fractions, such as <1.0 μm, <2.0 μm and 2.5 μm, and not with fractions $\geq$ 10 μm. Therefore, this indicates all the magnetic concentration parameters

could be used as a particle size proxy, particularly if the kinship is required with particles < $PM_{2.5}$, but it also indicates that χ_{LF} could be used if the kinship is required with a wider spectrum of particle sizes.

Table 3: Pearson's correlation coefficients (r) between mineral magnetic concentration and particle size parameters for urban roadside particulates (a) traditional sediment size fractions and (b) respiratory health-related size fractions (n = 50 samples).

(a)	Clay <2 μm	Silt 2-63 μm	Sand 63-2000 μm
χ_{LF}	0.701***	0.645***	-0.667***
χ_{ARM}	0.330*	0.372**	-0.378**
SIRM	0.338*	0.172	0.192

(b)	$<PM_{1.0}$	$<PM_{2.5}$	$<PM_{10}$
χ_{LF}	0.659***	0.705***	0.687***
χ_{ARM}	0.413**	0.298*	0.134
SIRM	0.315*	0.325*	0.236

Note: Significance levels: P <0.05 = *; P <0.01 = **; P <0.001 = ***

5 Discussion

Previous magnetic studies have noted significant correlations between χ_{LF}, χ_{ARM}, SIRM and particle size. To date, Oldfield *et al*. [15] has identified that anhysteretic remanent magnetisation (ARM) measurements can be used to reflect the concentration of fine-grained magnetite (<0.1 μm) in the clay fraction and low-frequency magnetic susceptibility (χ_{LF}) measurements can be used to infer the presence of coarser multi-domain magnetite (>1.0 μm) in sands and coarse silts. Clifton *et al*. [8] found χ_{LF} was strongly associated with sands and medium silts, susceptibility of ARM (χ_{ARM}) was strongly associated with clay and fine silts, and saturated isothermal remanent magnetisation (SIRM) was strongly associated with very fine to medium silts. Zhang *et al*. [16] suggested that both percentage frequency-dependent magnetic susceptibility ($\chi_{FD\%}$) and χ_{ARM} can be used as a proxy for clay content. However, more recently, Booth *et al*. [9] suggested χ_{LF}, χ_{ARM} and SIRM have potential as a particle size proxy for particular sedimentary environments, but highlight the importance of fully determining the nature of the relationship between sediment particle size and magnetic properties before applying mineral magnetic data as a size proxy.

These studies illustrated sand correlated negatively with χ_{LF} (r = –0.94), χ_{ARM} (r = –0.96) and SIRM (r = –0.91); silt correlated positively with χ_{LF} (r = 0.96), χ_{ARM} (r = 0.96) and SIRM (r = 0.96); and clay correlated positively with χ_{LF}

(r = 0.82), χ_{ARM} (r = 0.94) and SIRM (r = 0.81). When data presented here are compared to these earlier investigations, it is apparent that the trends observed are similar to previous studies (e.g. sand and χ_{ARM} (r = –0.38), silt and χ_{LF} (r = 0.65), clay and SIRM (r = 0.34)). The magneto-associations with each of the traditional sediment class sizes highlights the potential use of mineral magnetic data as a means of normalizing compositional analytical data (i.e. geochemical) for particle size effects.

The significant correlations between the magnetic parameters and the respiratory-health related size classes is perhaps of greater importance, because this highlights the technique as a possible alternative PM monitoring tool, which could be linked to both health and pollution studies. Given the combination of low-cost and sensitivity of the method, it can be argued that mineral magnetic measurements have considerable potential to act as a reliable particle size proxy. The method is also rapid; bulk samples require little preparation and individual measurements of magnetic susceptibility (χ_{LF}) can be made in ~1 minute, in either a laboratory or field setting. Therefore, it is feasible that mineral magnetic measurements could be a dependable and rapid exploratory technology for pilot urban roadside PM investigations.

6 Conclusions

Analyses indicate each of the magnetic concentration parameters could be reliably employed as a suitable particle size proxy for urban street dust. Of the three magnetic parameters, χ_{LF} has the strongest and most significant correlation values and, furthermore, is consistently significant ($P < 0.001$) with all class sizes. Moreover, theses data associations follow the predictable trends of other environmental studies. Therefore, given the speed, low-cost and sensitivity of the measurements, this suggests magnetic techniques could be used as a rapid alternative exploratory technology for pilot particulate pollution investigations.

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Trends in ozone levels and identification of visible injuries on agricultural crops in areas in the Metropolitan Zone of Mexico Valley

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Abstract

Measurements of ozone concentrations were carried out in the ambient air of agricultural areas of the Metropolitan Zone of the Valley of Mexico. Meteorological parameters, processes of synoptic scale and the possible damage to the agricultural crops were related to the ozone levels measured. The project was carried out in two campaigns: the first was carried out in the agricultural areas of the Parres, Tlahuac and San Luis, Xochimilco, in the Federal District from August 9 to August 28 of 2002; and the second was carried out in Huixquilucan, located at Mexico State, during June and July of 2003. The measurements were performed by continuous analyzers, whose principle of operation is the UV-Photometry. In the first campaign (2002), the analysis of the data showed maximum 1-hour concentrations of ozone up to 175 ppb, 169 ppb, and 192.7 ppb in Tlahuac, San Luis Xochimilco, and Parres, respectively. During the second campaign (2003), the maximum average 1-hour ozone concentrations found in Huixquilucan during June and July, were up to 172 ppb and 213 ppb, respectively. It was demonstrated that in the study areas during 2002 and 2003, the 1-hour concentrations of ozone reached harmful values for the agricultural crops. In the agricultural areas of San Miguel de Topilejo, characteristic damages attributable to ozone were identified in potato and oat cultivations.
Keywords: ozone concentrations, impact on crops, foliar damage, Mexico.

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1 Introduction

Photo-oxidant compounds like ozone have been a cause of concern around the world during the last years due to their effects on vegetation [9]. There is evidence that high concentrations of ozone cause different effects on vegetation, including visible damages to the foliar tissues, decreases in yield and growth rates in plants and a high sensitivity to biotic and non-biotic stress factors [18].

Some research works about exposure of plants from different communities at realistic levels of ozone have been reported, to assess the sensitivity of specific species to this pollutant to determine threshold values of damage and to propose secondary standards for protection to the vegetation [1, 6, 7, 10, 17].

In Mexico there are several studies about the assessment of the impacts of high ozone concentrations in some forested regions near Mexico City. The extensive forest decline in the mountains to the south-southwest of Mexico City has been associated with air pollution [2]. Symptoms of foliar photochemical injury to conifers and the local black cherry are severe in Desierto de los Leones, a protected area near the city [2, 3, 14, 16, 20]. However, injuries from air pollution to agricultural crops are less known [3, 13]. For this reason it is important to measure ozone concentrations in agricultural areas near Mexico City to determine if these concentrations reach values higher than those reported as dangerous for vegetation and to determine if these ozone levels affect the growth of cultivations in these regions. Likewise, it is important to correlate some meteorological phenomena in a synoptic scale to the ozone levels found in the study areas.

This study focuses on an analysis of ozone pollution in some agricultural areas near Mexico City, identifying ozone severe episodes and foliar injuries in specific species during August of 2002, and June and July of 2003.

2 Materials and methods

2.1 Study area

The first campaign of this study was carried out in agricultural areas of Parres, Tlalpan, Tlahuac and San Luis Xochimilco during August of 2002; and the second campaign was carried out in Huixquilucan, Mexico State during June and July of 2003. Table 1 gives a brief description of each monitoring site and the specific location of each monitoring site is shown in Figure 1.

2.2 Methods

For the current research, API model 400 ozone continuous analyzers were operated at each respective site. 10-min averaging time intervals were monitored and recorded in Parres, San Luis, and Huixquilucan. In the Automatic Atmospheric Monitoring Station of Tlahuac, 1-hr averages were monitored and recorded. All data sets were checked for anomalies and missing records.

Anomalies caused by calibration procedures, power problems, and so on, were removed from the data sets before statistical analysis.

Table 1: Description of the study area.

Monitoring Site	Description
Parres, Tlalpan	Located at 19º 17' N and 99º 10' W, ca. 2800 m with an extension of 308.71 km^2. The main crops cultivated in this area are oat, corn, and potato and there is an extensive forested area. The exact monitoring site was located in the facilities of the Natural Resources Commission (CORENA) of the Federal District Government.
San Luis, Xochimilco	Located at the Xochimilco Delegation, at 19º 16' N and 99º 06' W, ca. 2240 m with an extension of 119.16 km^2 [15]. In this area, the dominant crops include corn, radish and gourd. The monitoring equipment was located inside the facilities of the Natural Resources Commission (CORENA) of the Federal District Government.
Tlahuac	This specific monitoring site was located inside the Automatic Atmospheric Monitoring Station of Tlahuac, which belongs to the Automatic Atmospheric Monitoring Red (RAMA) of the Federal District Government at 19º 17' N and 99º 00' W. This area has a territorial extension of 86.36 km2 and 60% of the ecological conservation soils are dedicated to agricultural activities [15].
Huixquilucan, Mexico State	The monitoring equipment was located inside the facilities of the Family Integral Development (DIF) of the Federal District Government in San Cristobal town at 19º 24' N and 99º 18' W.

During the monitoring period, meteorological parameters were measured by a portable meteorological station (Met One, Autromet model) in Parres, San Luis and Huixquilucan. To determine ozone threshold values, 8-hr averages and 1-hr averages values were computed to determine how many times the air quality standard was exceeded during both campaigns. Likewise, ozone maximum concentration values were identified in each site. Additionally, it was carried out a synoptic meteorology analysis. Wind fields at the heights of 8000, 9000 and 10,000 ft were used. For the first campaign were used maps developed by the Automatic Atmospheric Monitoring Red (RAMA) of the Federal District Government at 12:00 Z (07:00 hr local time) and for the second, were used the maps developed by the Meteorological Service of Cuba, at 12:00 Z, 18:00 Z and 00:00 Z. Additionally during the observation on the ozone effects an adjacent area covered by pine forest was evaluated to know the health condition during

July of 2003, because damage caused by parasitic plants was observed, the 6-class rating system proposed [11] was used to evaluate the infection level, the live crown is visually divided into thirds, each third is rated as zero for no mistletoe visible, one when less half of the branches infected or 2 more than half of the branches infected, rating of each third and then added to obtain a total for the tree [12].

Figure 1: Location of monitoring sites in Mexico Valley.

An analyses correlation based on the data obtained from August 9 to 23, 2003, was made with the SAS program [19] from the averages obtained of the lectures hourly from 10:00 to 18:00 hours in Parres, San Luis, and Huixquilucan.

3 Results and discussion

During the first campaign (from August 9 to August 28, 2002) ozone maximum concentrations of 175 and 161 ppb were observed in Tlahuac and San Luis, respectively, On the other hand, in Parres, a maximum value of 187 ppb was registered (Figure 2). During the second campaign (from June 20 to July 14, 2003) ozone maximum concentrations values of 172 ppb and 213 ppb were found in Huixquilucan during June and July, respectively (Figure 3).

These values may cause severe damages to vegetation, and human health could be in risk, even when these sites are located far away from the center of Mexico City. It is possible that these ozone levels have their origin from transport of air pollutants from Mexico City. According these results, a classification was developed to indicate the air quality in agricultural areas

considered in this study. When ozone levels were higher than 80 ppb during eight continuous hours, air quality condition was classified as “an unacceptable condition”; whereas when ozone levels were lesser than 80 ppb, air quality condition was classified as “an acceptable condition”.

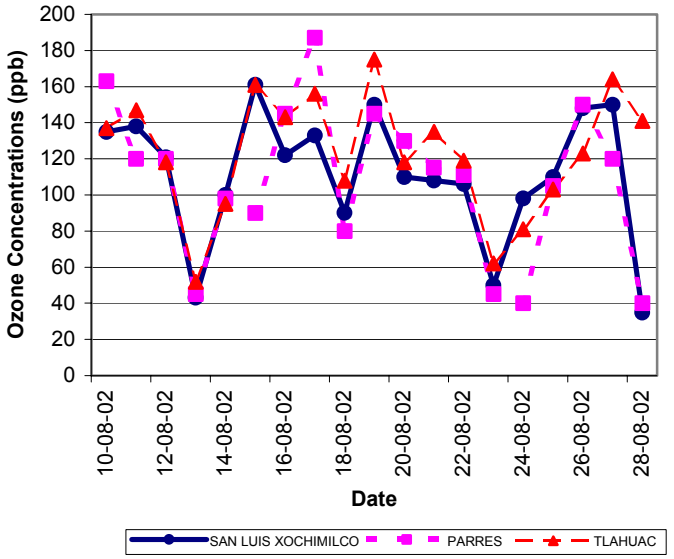


Figure 2: Daily maximum ozone levels during the first campaign.

In addition, it was registered the times when the air quality standard was exceeded in each site. The Mexican air quality standard [21] sets an 8-hr average concentration value of 80 ppb and a 1-hr average concentration value of 110 ppb. These values must not be exceeded more than once in a year. In Table 2, the classification of the air quality conditions is shown for each monitoring site.

Meteorological phenomena in a synoptic scale and local meteorology are related with pollutants dispersion in great urban centers where they are emitted as primary pollutants or formed as secondary pollutants, and also in agricultural zones, where these pollutants are transported from the urban centers.

During the first campaign, it was observed a relationship between hourly maximum ozone concentrations and meteorology, both, in a synoptic and local scales. In August 10, 2002, ozone levels kept under 10 ppb during the early morning (Figure 4), with a sustained variability of winds all the time. At 10:00 hrs, wind came from the north, and at this time, ozone concentrations increased, exceeding the threshold value to protect vegetation against damage for exposure to this pollutant. This wind direction kept sustained during seven hours, after this time period, once again it was observed a variability of winds, and ozone concentrations decreased. During the first campaign, according to figure 5, it can be observed that the wind during August 10, 2002, was due to a tropical wave located over Istmo de Tehuantepec causing that the wind fluxes over Mexico

Valley came from northwest and blew to southeast with a speed of 10 km h^{-1} (2.7 m s^{-1}) transporting air masses from urban zones toward the study area.

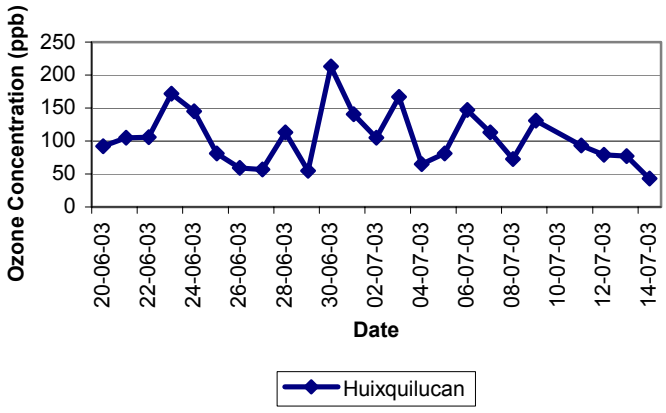


Figure 3: Daily maximum ozone levels during the second campaign.

Table 2: Classification of the air quality conditions for each monitoring site.

Monitoring Site	Classification of the Air Quality Conditions			
	Unacceptable Conditions Percentage	Acceptable Conditions Percentage	Data percentage that exceeded 1-hr average concentration value	Data percentage that did not exceed 1-hr average concentration value
First Monitoring Campaign (August 9-August 28, 2002)				
Tlahuac	18.3333	81.6667	0.2092	99.7908
San Luis, Xochimilco	6.8966	93.1034	4.3103	95.6897
Parres	3.3898	96.6102	4.8729	95.1271
Second Monitoring Campaign (June 20- July 14, 2003)				
Huixquilucan, Mexico State	8.1301	91.8699	2.7439	97.2561

The sites monitoring for ozone exposure indicate a 0.92 correlation coefficient this is a very good correlation between the conditions between San Luis and Parres while these two are not good related with the condition of Tlahuac with only 0.82 (R. $p < 0.01$)

During the morning, wind flow showed a calm period which prevailed and held high pollutants levels which transported from south-southwest to monitoring zone. For this reason, ozone concentrations reached maximum values exceeding 110 ppb during for hours (Figure 7).

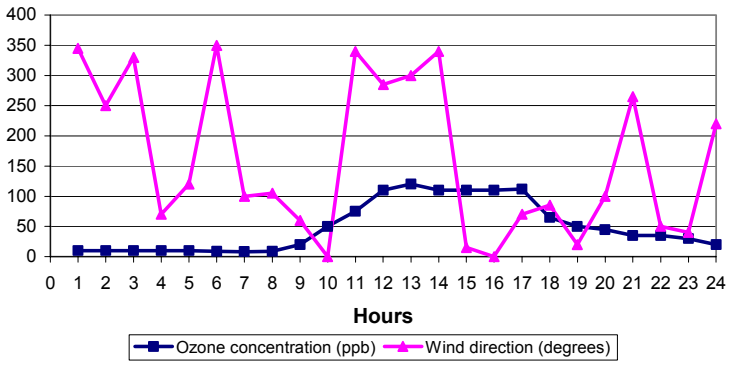


Figure 4: Hourly ozone concentrations and wind direction at San Luis-Xochimilco during August 10, 2002.

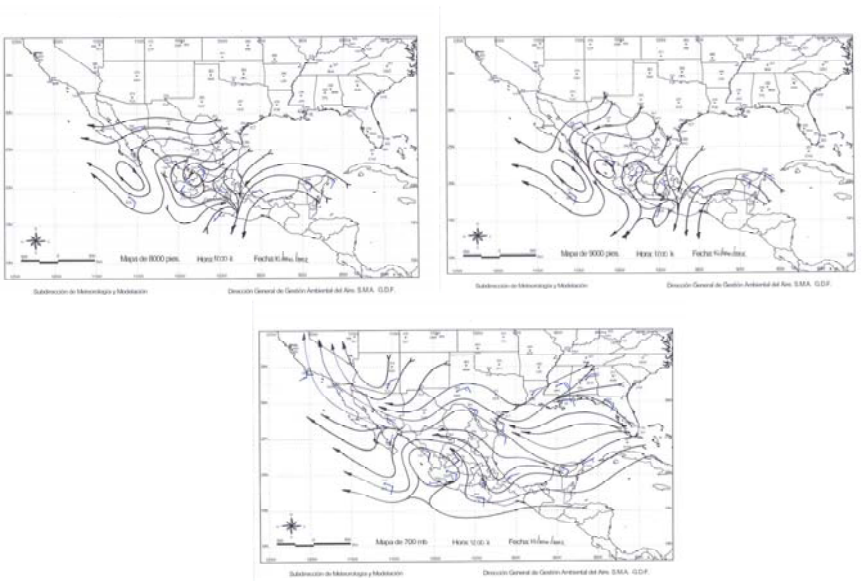
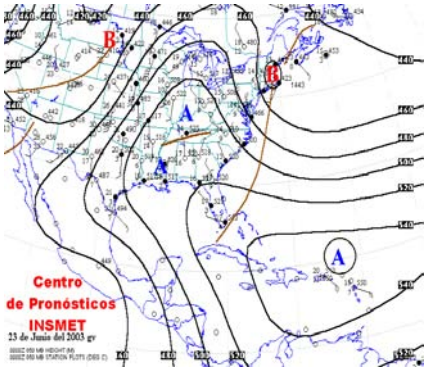


Figure 5: Wind Flux Analysis at 8000 ft (left upper map), at 9000 ft (right upper map) and 10000 ft (bottom center map) of height at 12:00Z during August 10, 2002.

Some agricultural areas in San Miguel de Topilejo are located surrounding the site where continuous analyzers were located. In this zone, some agricultural fields with crops of potato, corn, gourd, radish and oat were selected to identify visible damages. The injuries observed in gourd leaves and potato (Figure 8) showed a good agreement with typical characteristics reported by other

researchers for crops with wide leaves when these are exposed to high ozone levels [2, 3, 6, 7] .



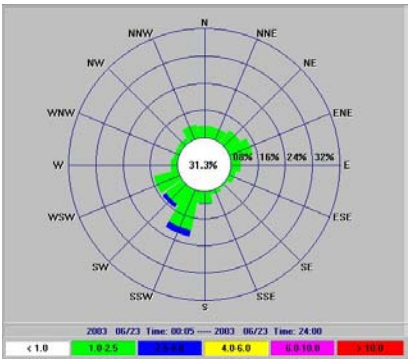


Figure 6: Synoptic analysis of upper air masses for June 23, 2003 for a height level of 850 hpa at 0000Z, and local windrose for Huixquilucan, Mexico State.

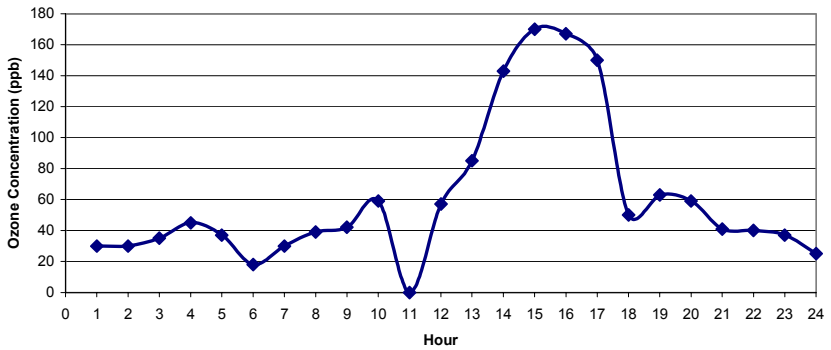


Figure 7: Hourly ozone concentrations at Huixquilucan, Mexico State during June 23, 2003.

The typical damage is irregular, bifacial, marginal and intervein, with necrotic areas, whitish dots, and chlorotic in aged leaves. When ozone levels are high, affected areas join each other to form greater burned areas and perforated zones. Similar damages were observed during the first and the second campaigns on crops of corn and oat.

The observed damages were attributable to high ozone concentrations; however, these damages contributed to the occurrence of pathogen organisms and the assessment of these indirect impacts requires additional research to determine their relative contribution to the total impact. In the forest area of Parres assessed to know the level infection of dwarf mistletoe was found and

identified as *Arceuthobium globosum* Hawksworth and Wiens occurring on *Pinus hartwegii* Lindley. In the forest, from an area about 772.42 ha. a total of 40.17 ha. were evaluated a severely affected by the mistletoes as well as 156.42 ha. with moderate level according with the six class system, this indicates a very important occurrence of the dwarf mistletoe. Reports cited previously showed that in the Mexico city valley, there are some forested areas covered by this specific pine *P. hartwegii*, distributed mainly in high elevation area and exposed to ozone from the Mexico city, the air pollution can predispose to dwarf mistletoe infection [5].

Figure 8: Visible Injuries due high ozone levels over agricultural crops of potato (left) and gourd (right).

Also some insect forest that affect the pines when they are considered as weakly trees especially bark beetles (*Dendroctonus* spp and *Pythiopthorus mexicanus*) were identified associated with the pines affected by mistletoes [8].

4 Conclusions

In agricultural areas of Xochimilco, Parres, Tlahuac and Huixquilucan, the ozone levels reached values higher than those reported as harmful for agricultural crops. From synoptic meteorological maps and local meteorology, it could be conclude that air masses were transported from Mexico City toward rural zones in the surroundings of Mexico State, suggesting that ozone was transported, and that the high ozone levels resulting caused injuries to agricultural crops, especially to sensible species like potato, gourd, corn and oat. Visible injuries identified showed a good agreement with those reported in other countries for sensitive crops exposed to ozone.

Acknowledgements

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A method for the characterisation of ambient dust: geochemical analyses of directional sticky pad dust samples

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Abstract

DustScan is a method of sampling ambient dust. It was developed at the University of Leeds as a low-cost technique for directional nuisance dust monitoring. It is a passive system that uses self-adhesive 'sticky pad' collection slides mounted on cylinders to collect dust in flux at quarries, waste facilities, etc. After typically 1–2 weeks the sticky pads are sealed with a transparent film then scanned on a flatbed scanner linked to a computer. Directional dust levels are quantified using specific software as Absolute Area Coverage (presence of dust irrespective of colour, AAC%) and Effective Area Coverage (darkness of dust, EAC%).

National Air Quality Standards (NAQS) require particular elements in air (e.g. Pb) to be assessed. Concentrations are usually determined using active monitoring equipment where dust, typically at a size convention (e.g. PM_{10}), is drawn onto a filter. Such methods may be non-directional and require a power supply. This paper describes the development of methods to characterise DustScan samples using ICP-OES and ICPMS, including determination of indicative elemental mass concentrations in air. Dust is not readily removed from the sticky pads and its mass is low in relation to the substrate. Sample preparation is based on 'total' digestion of the dust in using HF and HNO_3. Rigorous blank correction is important as some elements are at significant and variable concentrations in the sticky pads themselves. The analytical method has been refined to determine the mass of the mineral residue of the sample after ignition at 550°C. From this, plus duration of sampling and average wind speed, it is possible to estimate average concentrations of specific elements in ambient air by direction.

Keywords: ambient and directional dust, dust monitoring and characterisation, sticky pad, landfill.

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1 Introduction

'Dust' is defined in BS6069, Part 2, (British Standards Institution [1]) as particulate matter 1–75 μm in diameter, produced at mineral extraction sites mainly through the crushing and abrasion of minerals (ODPM [2]). Other properties such as shape, particle chemistry and physical behaviour in air can also be used to evaluate and characterise dust (Environment Agency [3]). Dust monitoring methods are described and discussed in detail elsewhere, such as in Monitoring Methods for Ambient Air: Technical Guidance Note M9 (Environment Agency [4]) or at www.goodquarry.com [5].

Dust sampled by different methods can be analysed using a variety of techniques. These range from tests that can be carried out on site, such as visual inspection, to laboratory analyses such as SEM-EDX and ICP-AES [3]. Dust characterisation through its analysis and speciation is a feature of Local Air Quality Monitoring for National Air Quality Standards (NAQS) (Defra [6]) and is an important aspect of air quality testing at sites such as landfills and waste transfer operations [3].

The physical and/or chemical properties of dust can be characterised through various analytical techniques. Different analytical methods are applied to dust characterisation according to the properties in question. Size fractions are determined gravimetrically with reference to CEN method EN 12341 [3]. Mineral fibres such as asbestiforms are assessed in accordance with health and safety legislation and guidance (HSE [7]).

Specific chemical elements in dust (e.g. Pb) are monitored as part of NAQS (DETR [8]). Increasing attention is being paid to concentrations of other elements (e.g. Cr, Ni, Cu, As and Cd) [3]. There are no standard methods for the chemical characterisation of dust although a draft CEN method for analysis of Cd, Ni, As and Pb in PM_{10} is being validated [3].

The cost, practicality and availability of equipment for dust sampling, and methods available for its characterisation are important considerations in air quality monitoring, and no standard method yet exists.

In the absence of a standard method for the chemical characterisation of dust in flux, a range of analytical methods to characterise directional sticky pad samples has been investigated including optical microscopy, SEM-EDX and ICP-OES (Datson and Fowler [9]). This paper documents the development of a new approach to chemical characterisation of ambient dust through ICP-OES/MS analyses of sticky pad directional dust samples, and outlines potential applications by briefly reviewing several case studies.

2 Dust sampling methodology

2.1 Directional dust sampling

Ambient dust was sampled with DustScan directional gauges, which use the 'sticky pad' method for dust monitoring. Sticky pad dust monitoring was popularised in the UK by Beaman and Kingsbury [10, 11]. The method is widely

used as a method for assessing potential nuisance caused by dust at quarries, landfill sites, opencast coal workings etc. Dust in settlement and in flux adheres to the adhesive surface of the sticky pad for subsequent quantification. Dust coverage is assessed as soiling effect either by using a hand-held reflectometer [3] or computer-based scanning (Datson and Birch [12]). The mass or particle size distribution of dust is not generally determined, although mass deposition can be estimated where particle size as cross-sectional area, density and reflectivity are known [11].

DustScan was developed at the University of Leeds for monitoring nuisance dust at opencast coal sites and quarries (Farnfield and Birch [13]). Further developments to the system have been carried out since 2001, firstly by The Geoffrey Walton Practice, Charlbury, Oxford, UK, and from 2004 by DustScan Ltd, Charlbury, Oxford, UK (Hull and Datson [14]).

DustScan is a passive dust monitoring system to monitor fugitive dust 360° around a replaceable sampling head. It uses a transparent, permanent adhesive, 'sticky pad' on a 70 mm diameter cylindrical monitoring head. The dust monitoring head is mounted on a stand and fixed approximately 2 m from the ground. The sticky pads are manufactured by specialist suppliers from stock material and comprise three principal layers: a transparent PVC film, a permanent, cross-linked polymer acrylic adhesive and a silicone-coated paper liner (Avery Dennison [15]).

The sticky pads are 297 × 219 mm and the paper liner is pre-scored to form a 217 × 178 mm sampling area. 6 mm diameter holes are pre-punched into the sticky pads to enable precise fitting to pegs on the cylindrical monitoring head. The paper liner is removed from the sampling area at the start of a monitoring period and the monitoring head samples continuously whilst installed in the field. Dust in flux impacts on the exposed section and is held on the adhesive surface. At the end of a sampling period, the monitoring head is removed and placed in a protective carrying flask and a replacement head fitted. Used sampling heads are normally sent to DustScan Ltd for processing. The remainder of the paper liner is removed from the edges of the sticky pad when the sample is sealed to enable encapsulation and to provide an unexposed 'reference area' for computer analysis [12]. The sticky pads are sealed with a standard A4 transparent PET office laser printer film. A typical field installation is shown in Figure 1.

Measurement of dust coverage on the sticky pads uses a computer-based scanning system and specific software. The pattern of dusting on the sticky pad indicates the direction and scale of potential dust nuisance by direction. Measurements are taken over 5° intervals around the cylinder and reported at 15° intervals by comparing the colour of the exposed area of the sticky pad with the unexposed, blank, 'reference area'. The results are normally reported in two nuisance dust measurements:

- Absolute Area Coverage (AAC%) – the presence of dust irrespective of colour;
- Effective Area Coverage (EAC%) – the darkness or potential soiling of dust.

Figure 1: An example DustScan monitoring installation.

EAC% is a 'custom and practice' nuisance measure. 5% EAC per day is considered a threshold for 'serious complaints' [3].

3 Dust analysis and characterisation methodology

3.1 Dust sub-sample selection

A diversity of AAC% and EAC% measurements are found in directional dust samples, according to dust coverage and dust type [14]. Hence it was considered that differences in directional dust observed in AAC% and EAC% measurements could indicate differences in dust composition. Selected sticky pad dust samples were sub-sampled for chemical analysis to investigate directional variations in ambient dust composition. Sub-sample selection was made at 15° intervals in correspondence with peak dust levels detected in the computer analysis.

The 217 × 178 mm sampling areas of selected sticky pads were sub-divided into 9 × 80 mm strips thus allowing 2 sub-samples per 15° interval and leaving a 9 × 18 mm reference section for retention.

3.2 Dust sub-sample preparation

Dust is not readily removed from sealed sticky pads and the cross-linked polymer acrylic adhesive is not soluble in common organic solvents (Datson [16]). Alternative, commercially-available adhesives are not necessarily transparent or UV-stable. UV-stability is necessary to prevent discolouration by sunlight which can affect some sticky pads and hence the potential soiling measurement of the sample (Merefield [17]).

Thus the dust was not removed from the sticky pads and the samples were prepared for ICP-OES/MS analysis (at the Universities of Gloucestershire and Portsmouth respectively) by 'total' digestion using HF and HNO_3 following an adaptation of standard procedures (Chao and Sanzolone [18]).

Each 9 × 80 mm sub-sample was placed in a clean, labelled, 25 cm^3 PTFE beaker to which 3 cm^3 concentrated analytical grade HNO_3 and 3 cm^3 concentrated analytical grade HF were added. Each sample was left to stand overnight then held at ≈100°C until incipient dryness. A further 3 cm^3 of concentrated HNO_3 were added carefully to collect any remaining HF, and evaporated to dryness. To take up the resulting salts, 3 cm^3 10% HNO_3 were added to each beaker which was agitated gently and again left overnight. The resulting solutions were carefully decanted into clean, labelled, 15 cm^3 centrifuge tubes. A final 2 cm^3 10% HNO_3 were added to the beakers and left to stand for approximately 2 hours, in order to dissolve any recalcitrant salts. These solutions were decanted into the appropriate centrifuge tubes, and stored ready for analysis by ICP-OES at a final volume of 5 cm^3. For ICPMS analysis the solutions were made up to 25 cm^3 and stored prior to analysis.

3.3 Dust sub-sample analysis

At the University of Gloucestershire, samples were analysed by ICP-OES using a Perkin-Elmer Optima 4300 dual view instrument. Calibrations were constructed using synthetic multi-element solutions, and analytical wavelengths were those suggested by the USEPA. Routine reproducibility tests confirm instrumental precision to be well within +/- 5%.

At the University of Portsmouth, samples were analysed by ICPMS using an Agilent 7500cs instrument equipped with an octopole reaction cell. Calibrations were again constructed using synthetic multielement solutions, and similar levels of instrumental precision are routinely attained.

The procedural detection limit of most elements with the method used for the analyses is estimated to be ca. 0.01 ppm in solution although the ICPMS equipment is considerably more sensitive than this, and its full capabilities are currently being explored. Samples at or below this limit are reported as 'bdl'. For sticky pads with typical dust loading, the detection limit equates to approximately 10 ppm in the dust, because of the dilution factor introduced during sample dissolution.

3.4 Sample blank-correction

Given the required dissolution method described above, it was recognised that the chemical composition of the dust sampling media might affect the results of the analyses. Therefore, the principal sticky pad components (PVC film with adhesive and PET sealing sheet) were analysed individually in a series of tests, and complete reagent blanks (i.e. including sticky pad reference area blanks) were run with each batch of unknown sticky pad samples.

Results of the analyses were given as ppm in solution. As the solution volume was uniform and the sub-sample area was known, the results of the analyses can be expressed as element mass per unit area. Summary values for a sample of sticky pad reference areas (blanks) are given in Table 1. The averages and ranges of concentrations are shown in Figure 2.

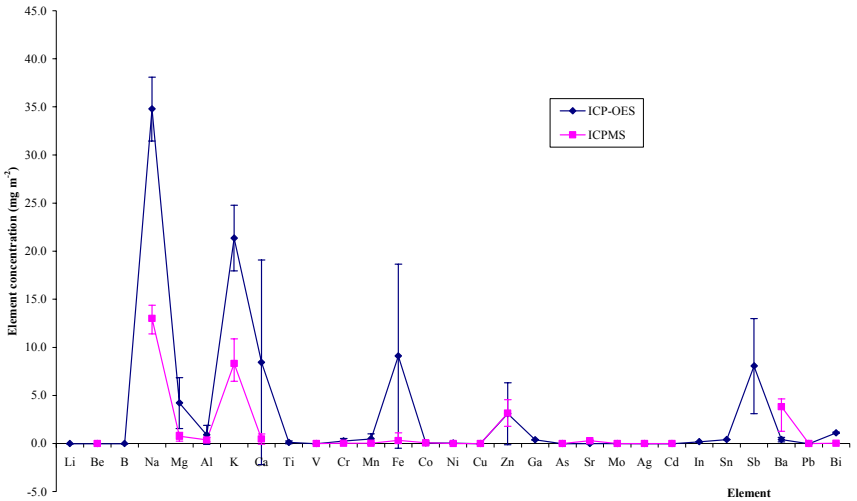

Figure 2: Line chart of averages and ranges of element concentrations in sticky pad reference areas as detected by ICP-OES and ICPMS.

The results of the reference area analyses indicated that certain elements were at relatively high and variable concentrations in the sticky pad components. Importantly, however, elements of interest to air quality monitoring such as Pb, As and Cd were either found at very low concentrations or below detection limits. Differences were noted in the concentrations detected by ICP-OES and ICPMS. The bulk of differences in element concentrations detected between the two methods were considered unlikely to be due to significant differences between the instrumental processes. Therefore it was considered likely that there was significant variability for specific elements in the composition of the sticky pads, such as between batches of the components manufactured.

Table 1: Summary values of sticky pad reference area (blank) analyses, mg m^{-2}, by instrument.

	ICP-OES (n = 7)					ICPMS (n = 12)				
Element	Average	Minimum	Maximum	Range	StDev	Average	Minimum	Maximum	Range	StDev
Li	bdl	bdl	bdl	N/A	N/A		-	-	-	-
Be	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
B	bdl	bdl	bdl	N/A	N/A		-	-	-	-
Na	34.79	32.13	38.10	5.97	2.44	13.02	11.39	14.37	2.98	0.80
Mg	4.23	2.15	6.87	4.72	1.75	0.76	0.25	1.17	0.92	0.42
Al	0.91	0.50	1.91	1.41	0.47	0.37	0.17	0.63	0.46	0.13
K	21.38	19.22	24.80	5.57	2.07	8.33	6.47	10.88	4.42	1.29
Ca	8.47	5.72	19.10	13.39	4.82	0.49	-0.08	1.00	1.07	0.40
Ti	0.15	0.08	0.30	0.21	0.08		-	-	-	-
V	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
Cr	0.29	0.11	0.55	0.44	0.17	0.03	0.01	0.06	0.05	0.01
Mn	0.49	0.03	1.02	0.99	0.36	0.03	0.01	0.05	0.04	0.01
Fe	9.11	4.07	18.68	14.61	5.03	0.32	0.03	1.12	1.09	0.37
Co	0.09	0.00	0.29	0.29	0.11	0.08	0.07	0.10	0.03	0.01
Ni	0.07	0.00	0.20	0.20	0.08	0.01	0.00	0.01	0.01	0.00
Cu	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
Zn	3.12	1.30	6.34	5.05	1.82	3.17	1.81	4.56	2.75	0.76
Ga	0.40	0.38	0.43	0.06	0.02		-	-	-	-
As	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
Sr	0.02	0.01	0.04	0.03	0.01	0.30	0.13	0.36	0.24	0.06
Mo	0.02	0.00	0.05	0.05	0.02	bdl	bdl	bdl	N/A	N/A
Ag	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
Cd	bdl	bdl	bdl	N/A	N/A	bdl	bdl	bdl	N/A	N/A
In	0.21	0.18	0.23	0.04	0.01		-	-	-	-
Sn	0.43	0.41	0.46	0.04	0.01		-	-	-	-
Sb	8.08	4.93	13.02	8.09	2.95		-	-	-	-
Ba	0.43	0.21	0.67	0.46	0.16	3.84	1.27	4.63	3.36	0.86
Pb	bdl	bdl	bdl	N/A	N/A	0.01	0.01	0.01	0.01	0.00
Bi	1.14	1.11	1.21	0.10	0.04	0.03	0.02	0.07	0.05	0.02

From the range of values obtained in the blank sticky pads it was considered that the concentrations of specific elements, particularly those found at low concentrations in ambient dust, could be 'masked out' by elevated concentrations in the sticky pads themselves. Hence it is accepted that the certain elements are currently unlikely to be analysed in the directional dust samples to a satisfactory level of confidence. Zn, Sb and Ba were found in high concentrations in the sticky pad components yet are environmentally relatively uncommon. Blank-correction for these elements could lead to unreliable reading in the directional samples, and results for these elements are normally rejected from the analytical data set.

However for the majority of elements blank correction is valid. Environmentally abundant elements, such as K and Fe are unlikely to be at such low concentrations in ambient dust to be masked by the sticky pads. The majority of elements analysed are found at low or below detectable levels in the sticky pads. Thus even low concentrations of elements such as Pb, Cd and As found in directional dust samples are likely to have originated in the dust sample as opposed to the sticky pad.

Thus the routine procedure applied to directional dust sample analysis includes analysis of a sample 'blank', analogous to the computer scanning methodology. A 9 × 80 mm strip is taken from the unexposed reference area of each sticky pad sub-sampled and is analysed in parallel to the selected directional dust samples.

3.5 Validation of the analytical method

As noted above, instrument precision was routinely determined to be better than +/- 5% with both instruments for all elements.

To determine the accuracy of the whole procedure, replicate samples of certified reference materials (CRM) were run with the batches of sticky pad sub-samples. In the absence of appropriate reference dusts, rock and soil powder CRM were used. In order to mimic sticky pad dissolution as closely as possible, several CRM-dosed sticky pad 'samples' were made as follows. A standard, stock, DustScan sticky pad was laid flat on a bench and the paper liner removed from the sampling area. NIST SRM2710 Montana soil (National Institute of Standards and Technology [19]) and USGS reference rock SCo-1 were scattered by hand onto the sampling area from approximately 15 cm through a 75 μm screen. The sticky pad was dusted until powder did not adhere further. The sticky pads were held perpendicular to the bench and tapped lightly to distribute any powder not adhering to the sticky pad and to remove excess. The sticky pads were sealed in the same manner as normal DustScan samples with a PET film and sub-sampled for analysis in the normal way.

Table 2: Recommended values for reference materials and average results of analyses by ICP-OES and ICPMS, after blank-correction.

	Montana SRM2710			USGS SCo-1		
Element	Recommended Values	ICP-OES average (n=8)	ICPMS average (n=3)	Recommended Values	ICP-OES average (n=8)	ICPMS average (n=2)
Ag	35.3	18.9	33.9			
Al	64400.0	64400.0	64400.0	72328.0	72328.0	72328.0
As	626.0	599.9	549.1	12.0	30.0	7.3
Ba	707.0	1605.0	1349.5	570.0	2081.4	1746.2
Be				1.8	0.1	0.5
Ca	12500.0	13121.4	13443.7	18728.0	20836.7	17182.5
Cd	21.8	21.2	14.7			
Co	10.0	12.5	6.2	11.0	13.8	6.1
Cr	39.0	23.3	41.8	68.0	46.9	61.3
Cu	2950.0	2783.1	2455.4	29.0	8.7	25.6
Fe	33800.0	31582.0	33773.4	35874.0	35188.7	36409.5
K	21100.0	22082.5	28113.3	22987.0	25871.0	29467.6
Mg	8530.0	13548.2	6803.4	16405.0	24602.4	28825.9
Mn	10100.0	9763.8	10473.1	410.0	388.4	405.2
Mo	19.0	17.8	15.0			
Na	11400.0	7918.6	16965.6	6594.0	4665.5	5956.7
Ni	14.3	9.0	11.1	27.0	14.0	12.5
Pb	5532.0	4838.9	4760.9	31.0	8.3	30.3
Ti						
Sr	330.0	244.2	319.7	170.0	118.5	94.0
V	76.6	72.0	65.6	130.0	133.6	121.2
Zn	6952.0	5061.5	3376.1	100.0	274.9	366.9

The quoted reference values for the CRMs and the average solution concentrations derived from the analyses of the prepared sticky pad samples are given in Table 2. Analyses are given after correction for the most appropriate reagent blank. Since individual sample masses were not available, in order for

such comparison to be made the data have been normalised to equality of Al concentration and assessment of data for all other metals made on that basis.

The average values are plotted against their recommended values in Figures 3 and 4. Error bars of +/- 25% have been added to the ICP-OES data and +/- 20% for ICPMS data, within which lies the 1:1 equiline for most elements.

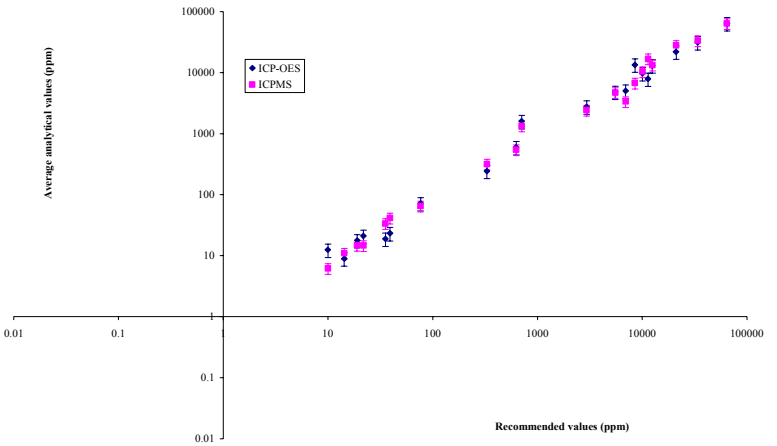

Figure 3: Scatter plot of average element concentrations determined by ICP-OES (error bars +/-25%) and ICPMS (error bars +/-20%) versus recommended values for NIST SRM2710 Montana Soil.

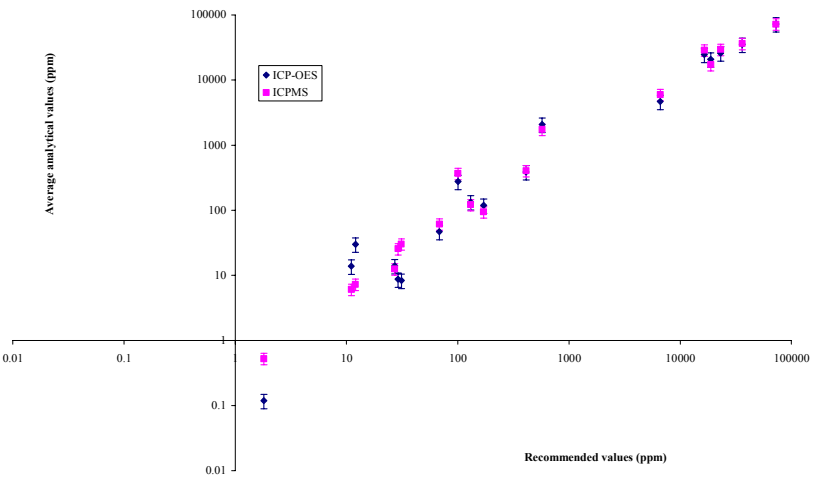

Figure 4: Scatter plot of average element concentrations determined by ICP-OES (error bars +/-25%) and ICPMS (error bars +/-20%) versus recommended values for USGS reference rock SCo-1.

3.6 Estimation of dust 'mineral mass'

Continued experimentation subsequently revealed that the substrate could be removed from the dust sub-samples by controlled ignition in air. To test this, sub-samples from samples taken at a landfill site and a limestone quarry were tested for losses on ignition together with a sample prepared with Montana soil.

Sections from unexposed reference areas and from the visibly dusted areas of sticky pads were cut, measured, weighed into porcelain crucibles and placed in a furnace at 550°C for 15 minutes. Details of selected sub-samples and weights before and after ignition are set out in Table 4 and plotted for comparison in Figures 5 and 6.

It was found that although the sampling media represented a significant proportion of the mass of sticky pad directional dust samples, the majority of the sticky pad was removed by controlled ignition. The residual mass is likely to represent the 'mineral' mass of the dust sample, which is therefore the fraction of the dust sample analysed by ICP-OES/MS.

Those part/s of the dust samples lost during ignition are likely to represent 'organic matter', such as dust from vegetation and small invertebrates adhering to the sticky pad. As C, N, H and O are the main constituents of such material and are not detected in the ICP-OES/MS analysis the removal of organic matter from the mineral mass is considered unlikely to adversely affect the inorganic characterisation of directional dust by this method.

Table 3: Results of loss on ignition test: sample mass details (g) and sample coverage (g m^{-2}).

Sample reference no.	Test sample description	Area (mm^2)	Crucible (g)	Crucible + sample (g)	Derived mass (mg)	Mass/area (g m^{-2})	Crucible + residue (g)	Derived residue mass (mg)	Residue mass/area (g m^{-2})	Blank-corrected mass (dusted section less reference area, mg)	Blank-corrected residue mass/area (g m^{-2})
00024	Ref. area 1	1374	11.9566	12.3400	383.4	279.08	11.9575	0.9	0.66	0.0	0.00
00028	Ref. area 2	1328	12.3777	12.7483	370.6	279.04	12.3780	0.3	0.23	0.0	0.00
00032	Ref. area 3	1484	14.7218	15.1001	378.3	254.98	14.7227	0.9	0.61	0.0	0.00
00036	Ref. area 4	1335	11.4865	11.8412	354.7	265.71	11.4871	0.6	0.45	0.0	0.00
00107	Ref. area 5	3059	12.6289	13.4623	833.4	272.48	12.6304	1.5	0.49	0.0	0.00
00110	Ref. area 6	3007	11.6981	12.5065	808.4	268.85	11.6994	1.3	0.43	0.0	0.00
00147	Ref. area 7	720	11.7740	11.9795	205.5	285.42	11.7742	0.2	0.28	0.0	0.00
00025	Dust area 1	1329	12.6671	13.0518	384.7	289.53	12.6728	5.7	4.29	4.8	3.61
00029	Dust area 2	1392	15.7760	16.1520	376.0	270.03	15.7773	1.3	0.93	1.0	0.72
00033	Dust area 3	1392	12.7014	13.0564	355.0	255.11	12.7027	1.3	0.93	0.4	0.29
00037	Dust area 4	1351	12.6312	12.9909	359.7	266.17	12.6344	3.2	2.37	2.6	1.92
00108	Dust area 5	5255	11.7740	13.1674	1393.4	265.17	11.7781	4.1	0.78	2.6	0.49
00111	Dust area 6	5442	11.4840	12.9454	1461.4	268.56	11.4875	3.5	0.64	2.2	0.40
00150	Dust area 7	720	15.8496	16.0589	209.3	290.69	15.8516	2.0	2.78	1.8	2.50

From these trials it was considered that differences in mass per unit area of the samples can be reliably observed after ignition and that the mass of the dust sample analysed by ICP-OES/MS can reasonably be inferred.

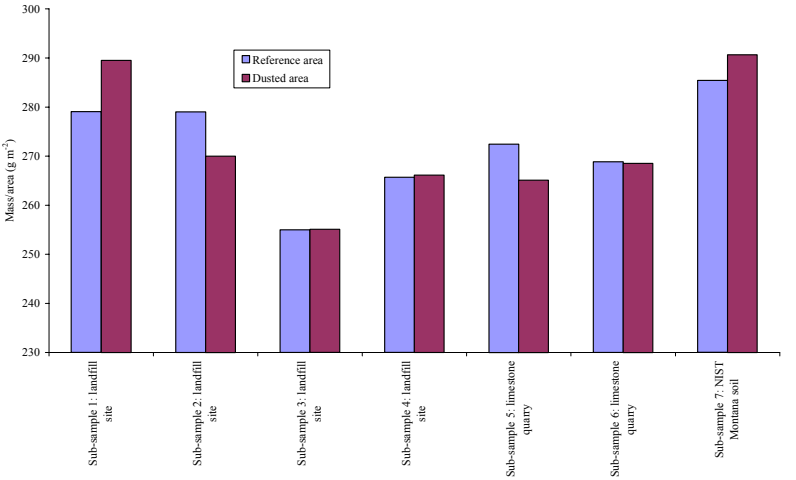

Figure 5: Comparison between mass/area of blank and dusted sticky pads: sample before ignition.

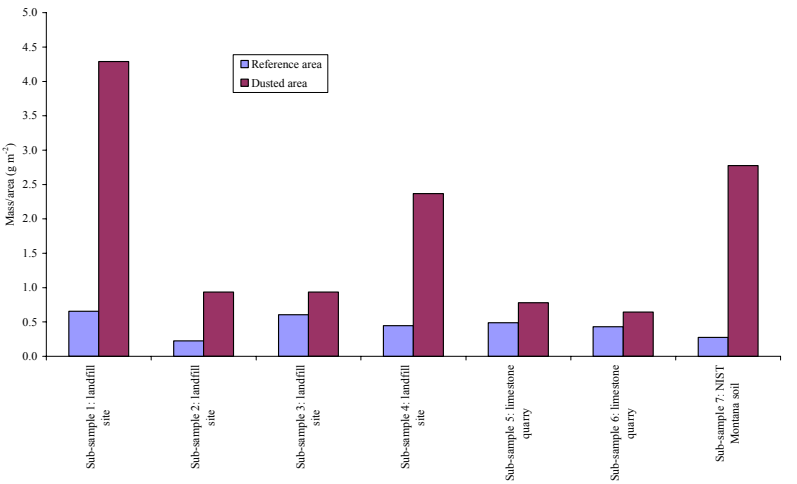

Figure 6: Comparison between mass/area of blank and dusted sticky pads: sample after ignition.

3.7 Estimation of element concentrations in directional dust samples

As it was found that sticky pads were largely eliminated by the ignition procedure, experimentation with sample size showed that 9 × 80 mm strips of sticky pad generally yield sufficient dust mineral residue to obtain a readily quantified mineral mass. As a 15° sub-section of sticky pad is 9 mm wide, 2 no. 9 × 80 mm strips and one 9 × 18 mm section are available for each 15° directional dust sample. ICP-OES/MS analysis may be carried out using one of the 9 × 80 mm strips. The parallel 9 × 80 mm strip, from the same 15° sampling direction, can be used to obtain the dust mineral mass. Assuming the directional samples are vertically homogeneous at this scale it is reasonable to consider that the mass per unit area of the ignited strip equates that of the strip analysed by ICP-OES/MS. Therefore element concentrations in the directional dust samples can be estimated from the mineral mass and the element concentrations in solution.

Many directional dust samplers are installed at sites where weather data are also recorded. An estimate of the directional 'wind run' can be determined as the perpendicular component of wind velocity in relation to the directional sampling surface with time, expressed as a linear value (m). Thus it is possible to infer the dust mass concentrations and element concentrations in ambient air during the sampling period. As the area of the directional sub-samples is known, both the dust mass concentration and the element mass concentrations can be determined. Whilst it is accepted that the values derived are time-integrated and approximate, it is considered that they may be of value as relatively low-cost, flexible and useful guides to aid local air quality assessment and monitoring.

4 Conclusion

The methodology described above is still being developed, but has reached the stage where reliable chemical information may be gathered from dust samples which have been collected on a directional basis. This opens the way to construction of dynamic dust flux models from sites at which sufficient monitoring takes place. Given the increasing stringency of environmental legislation, and the desire for sustainable use of resources, monitoring of this type is likely to become more important. Latest modifications suggest that an indication of average ambient air concentrations is possible, also on a directional basis, which could fulfil present and future regulatory requirements. In order to illustrate some of the potential applications of the method, a few brief case-studies are presented below.

4.1 Case study 1: limestone quarry

Residences near a limestone quarry in North Wales were affected by nuisance dust that was believed to have originated at the quarry. DustScan directional gauges were installed on the perimeter of the quarry and near the homes of the

residents. AAC% and EAC% data from the gauges at the residences showed that dust propagated towards the quarry as well as away from it.

Sub-samples were taken from sticky pad samples taken at the quarry boundary and at the residences. The sub-samples at the houses were taken from the direction of the quarry and from the opposite direction.

The sub-samples were analysed using ICP-OES. Dust at the quarry boundary had higher levels of Ca than from either direction at the residences. Dust from the direction of the quarry at the houses had more Ca than from the opposite direction. Concentrations of Fe were higher from the opposite direction to the quarry and concentrations of Na were greater from either direction at the houses than at the quarry.

However concentrations of most elements were more similar between the samples from either direction at the residences than between the quarry and the residences.

Therefore it was concluded that not all the dust at the residences had originated at the quarry, and that there was a significant background dust source that was contributing to dust at the residences.

4.2 Case study 2: landfill site 'A'

DustScan directional dust gauges were installed at a landfill site in Cambridgeshire. The site operator wanted to know if remediation works on a cell at the site might lead to emissions of identifiable dust from the cell.

Directional sticky pad dust samples were sub-sampled from a range of locations on the site perimeter. The sub-samples were analysed for a range of elements using ICP-OES.

The highest concentrations of Al, Mn, Cu and Pb were found in samples nearest downwind of the remediation works. The lowest concentrations of Pb were found upwind of the remediation.

The results of the analyses were compared using enrichment factors, which is an established method for analysis and comparison of aerosols (Rahn [20]). The EF of an element is calculated as the relative concentration of an element in a sample proportionate to its relative concentration in the earth's crust. EFs are determined in relation to an abundant element and for crustally-derived aerosols, this is typically Al, hence the EF for Al in all samples is 1.00.

Although the highest concentrations of Al were found nearest the remediation works, EFs for Mn, Cu and Pb were also higher at this location. From the results of the analyses and comparison of EFs it was concluded that dust nearest the remediation works was different to dust at other locations on the site and from elevated levels of, in particular Cu and Pb, was likely to have originated from the landfill cell.

4.3 Case study 3: Dolerite quarry

DustScan gauges were installed at a Dolerite quarry in Cornwall. Rocks in the region of the quarry are known to contain variable and high concentrations of

As. Consequently it was considered that dust propagating from the quarry could contain significant concentrations of As.

The directional dust gauges were installed within the quarry workings and on nearby farmland. Directional AAC% and EAC% measurements indicated that some of the dust sampled at the quarry could have propagated from the farmland as well as the quarry.

Directional dust samples were selected for analysis according to dust direction and monitoring location. Loose soil samples (grab samples) were also collected from the ground surface in the vicinity of 3 of the directional gauges. The soil samples were sieved to <75μm to obtain the dust fractions.

To test the accessibility of As in the directional samples and the soil dust samples the analytical method was modified. Sequential extractions were carried out using ultrapure H_2O, 0.5M HNO_3 and 'total' digestion in HF as normal. Only directional samples with sufficient dust coverage to enable the PET covering film to be removed from the sticky pad were selected for analysis. Blank-correction was carried out for the sticky pads at each extraction stage.

In the ultrapure H_2O extraction As was below detection limits in the sticky pad samples and low concentrations were found in the soil dusts. As was detected in both sample sets in the 0.5M HNO_3 extraction. The highest concentrations of As were found in both sample sets in the HF extraction. Higher levels of As were found in the directional and soil dust samples from the quarry than from the farmland. However a greater proportion of the As from the farmland was extracted in the ultrapure H_2O and 0.5M HNO_3 extractions. It was considered that these extractions would be likely to comprise bioaccessible As. A 'bioaccessibility ratio' of (ultrapure H_2O extraction plus 0.5M HNO_3 extraction) divided by (ultrapure H_2O extraction plus 0.5M HNO_3 extraction plus HF extraction) was derived which showed that As was more bioaccessible in the dusts from the farmland than from the quarry.

4.4 Case study 4: landfill site 'B'

DustScan directional dust gauges were installed on a landfill site in Gloucestershire. The site disposes of air pollution control residue (APC). Sub-samples of the directional dust samples were taken both upwind and downwind of the site to evaluate possible changes in air quality across the site.

Sub-samples of the sticky pad samples were analysed by both ICP-OES and ICPMS. It was found that dust coverage on the sticky pads was of significance in reliable analysis of the directional dust samples. Where dust coverage was low, generally as indicated by low AAC% levels, many elements were masked out by the sticky pad blank. Consequently it was considered that where AAC was less than 50% there was insufficient dust for reliable ICP-OES/MS analysis.

The mineral mass of many of the directional samples was determined by controlled combustion of parallel 15° sub-samples. Weather data were supplied by the site operator, as were analyses of the APC residues disposed of at the site during the intervals when directional samples were analysed. Local soils and clays used for cell engineering were sampled and analysed by ICPMS. The APC

analyses and the soil and clay analyses were considered to be local reference materials.

Observations were made from the directional sample analyses regarding possible changes in dust composition (and therefore air quality) across the site and in relation to other dust-producing operations in the vicinity.

Concentrations of dust mineral mass and inferred directional concentrations of elements in the dust were calculated from the results of the analyses and the weather data. The analyses of the directional samples were compared with the analyses of the APC residues and local soils and clays. It was considered that the local soils and clays and APC residues could comprise the end members of dust sampled at the site.

Ratios were calculated between pairs of elements selected to maximise the differences between the local soils and the APC residue. Data for all directional dust samples with sufficient dust coverage defined a binary mixing line between the end members, from which the APC component of any sample could be estimated. This approach could be applied to a range of settings where assessment of dust propagation from a particular source or activity is desired.

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NO_x adsorbent formulation research by uniform design

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Abstract

In order to develop a nitric oxides adsorbent, some kinds of natural minerals were used in the presented study. A series of adsorbents were prepared according to uniform design and the adsorbing abilities were determined. The regression equations were drawn and the best formulation named JA was obtained from the equations. JA was prepared according to the formulation, and the adsorbability was also determined. Results showed that the absorbent JA can adsorb 156.7mg of NO and 289.9mg of NO_2 simultaneously in 3 hrs and the saturated adsorption quantity of NO_x is 22.2% in experiment conditions, which is far better than that of active carbon. Comparing with traditional orthogonal design, experiments designed by uniform design can attain the purpose by fewer experiments. It can also obtain quantitative regression equations accurately on the basis of the results of the experiments. The equations are also helpful in results analysis.
Keywords: formulation experiment design, uniform design, NO_x adsorbent.

1 Introduction

Most NO_x in the atmosphere exist as NO and NO_2. The NO_x produced by human activity are primarily discharged from flue gas and secondly from chemical processes; for instance, nitric acid production, nitration process, explosive material production and nitric acid pickling process. In the above mentioned chemical processes NO_x is always discharged together with nitric acid mist.

There are many researches on NO_x in flue gas, such as selective catalysis reduction (SCR), selective nocatalysis reduction (SNCR), etc. This presented study is aimed at the NO_x of low concentration discharged from chemical processes.

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2 Materials and methods

2.1 Natural minerals as the raw materials

Many natural minerals with porous, stratified or catenarian structures have good adsorbing ability, such as bentonite, sepiolite, zeolite, kaolinite, etc. Because of their low cost, more and more researches on natural minerals are being carried out in the field of environment protection research. Adebowale et al. [1] modified kaolinite clay mineral with orthophosphate to adsorb Pb and Cd ions from aqueous solutions of the metal ions. Sanchez-Martin et al. [2] studied the efficiency of a series of clay minerals (montmorillonite, illite, muscovite, sepiolite and palygorskite) modified with the cationic surfactant octadecyltrimetylammonium bromide (ODTMA) in the adsorption of the pesticides penconazole, linuron, alachlor, atrazine and metalaxyl. Tahir and Rauf [3] studied the ability of bentonite to remove malachite green from aqueous solutions.

In this paper, three kinds of minerals zeolite, bentonite and attapulgite (marked as A, B and C respectively) were selected as the raw materials of the adsorbent. They were mixed with slaked lime (marked as D) to produce composite adsorbent. The adsorbent formulation was acquired by the specific design of experiment and the determination of the adsorb abilities.

2.2 Experiment design method

Formulation designs are commonly used in many industry processes and science researches. In these cases, the quality of the production is not determined by the total amount of the ingredients but by the proportion of them. Therefore, the essential work in formulation experiment design is to determine the relationship between the formulation and the experiment index through the selected experiment points. Basing on the experiment results the best formulation can be finally acquired.

In this paper, the study is aimed to obtain an optimized proportion of the raw materials A, B, C and D (as mentioned above) for the final absorbent, using the method of formulation design.

Many kinds of formulation experiment design methods are available, such as simplex–lattice design, simplex–centroid design, etc. [4]. Since the experiment points of simplex–lattice design and simplex–centroid design are not distributed uniformly in the experiment range and the boundary points are in the majority, uniform design which was invented by Chinese mathematicians Fang Kaitai and Wang Yuan was singled out for this study. It can conquer the shortcomings of other methods.

The experiments were designed as an unconstraint formulation design. The selected raw materials A, B, C and slaked lime (D) were considered as four factors of the experiments. In order to obtain a good regression result, the amount of experiments can not be less than two times of the number of the factors, reasonably, 3~4 times, thus every factor was divided into 12 levels.

Table $UM_{12}^{*}(12^{4})$ was selected and the 12 formulations of the adsorbents were listed in Table 1. The values of x_1, x_2, x_3 and x_4 represent the weight percentage of slaked lime (D) and mineral A, B, C in the adsorbent formulation respectively.

Table 1: Design of adsorbents formulations.

Serial No.	formulation			
	x_1	x_2	x_3	x_4
1	65.3	11.2	4.89	18.6
2	50.0	1.05	22.4	26.5
3	40.7	23.0	25.7	10.6
4	33.7	4.28	59.4	2.58
5	27.9	33.2	4.87	34.1
6	22.9	8.50	25.7	42.9
7	18.5	44.3	23.3	14.0
8	14.5	13.5	63.0	8.99
9	10.9	57.6	1.31	30.2
10	7.49	19.4	21.3	51.8
11	4.35	76.1	10.6	8.95
12	1.41	26.0	57.4	15.1

2.3 Preparation of the adsorbent

Mix the raw materials together according to the proportions listed in Table 1, then add some water and stir into mud. Shape the mud into pillared granules with the diameter of 2mm. After the granules were dried and activated by calcining the final adsorbent is produced.

2.4 Determination of the adsorb abilities

For the convenience in using the bench-scale system, the final adsorbent was broken and sieved so as to get the granules with the diameter of 1~1.6 mm. Stuff the sieved granules to a tubular adsorber with the inside diameter of 13.86 mm and the length of 180 mm. The adsorbent was stuffed to 12 cm high in the adsorber. The experiment system is shown in Figure 1.

The inlet gas is a mixture of NO and air. A part of NO will react with O_2 in the air to NO_2, thus there are actually NO, NO_2 and air in the inlet gas. The humidity of the gas was adjusted by a humidity control system. The outlet gas was discharged through an absorption bottle filled with NaOH solution. The concentration of NO and NO_2 were analyzed by Monitor Labs 8840 NO/NO_x Analyzer.

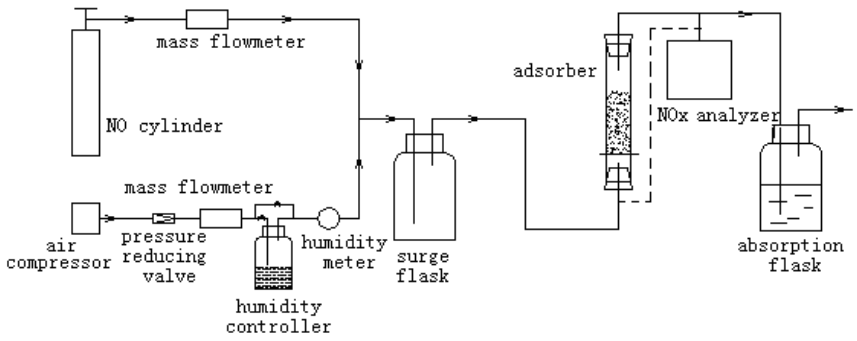

Figure 1: System for adsorb ability determination.

Table 2: Results of NO_x adsorption quantity in 3 hrs.

No.	adsorption quantity in 3 hrs (mg)	
	NO,y_1	NO_2,y_2
1	107.60	275.51
2	96.75	269.84
3	88.15	270.46
4	84.62	264.54
5	88.31	275.63
6	74.73	265.65
7	68.38	264.66
8	46.37	259.98
9	57.70	253.94
10	14.06	238.05
11	25. 15	243. 23
12	−39. 29	229. 18

3 Results and discussion

3.1 Adsorption quantity of NO_x in 3 hrs

Adsorption quantity of NO_x can be calculated by integral operation on the differences between the concentrations of inlet and outlet.

The inlet concentrations were: NO: 599mg/m^3 (447ppm), NO_2: 891 mg/m^3 (434ppm). The ambient temperature was 29~31°C. The relative

humidity was controlled between 69% and 71%. The space velocity was 6000 h^{-1}. The results of NO_x adsorption quantity in 3 hrs is listed in Table 2.

Based on the data of Table 2, the following regression equations were acquired using SPSS software:

$$y_1=0.064x_1x_2+0.039x_1x_3+0.038x_1x_4-0.020x_2x_3 \quad (1)$$

$$y_2=1.958x_1+2.328x_2+2.480x_3+2.241x_4+0.027x_1x_2 +0.015x_1x_3+0.034x_1x_4-0.009x_3x_4 \quad (2)$$

where y_1 is the NO adsorption quantity (mg) in 3 hrs, and y_2 is the NO_2 adsorption quantity (mg) in 3 hrs.

Obviously:

$$x_1+x_2+x_3+x_4=100 \quad (3)$$

Solve the systems of equations constituted of eqn. (1), (3), and eqn. (2), (3) using Microsoft Excel. The following results can be acquired: for the variables x_1=50, x_2=50, x_3=0, x_4=0, a maximum of y_1 occurred at 160mg; and for x_1=45.84, x_2=54.16, x_3=0, x_4=0, the maximum of y_2 occurred at 295.54mg.

3.2 Comparison of the adsorb abilities between NO and NO_2

No.1 adsorbent is the best one of the 12 adsorbents in Table 2 by intuitive analysis. The removal efficiency of NO and NO_2 by No.1 in 3 hrs were compared in Figure 2.

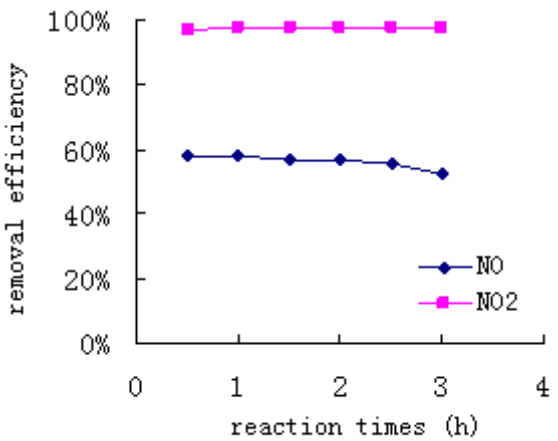

Figure 2: Comparison of removal efficiency between NO and NO_2.

It can be seen in Figure 2 that NO_2 is far easier to be removed than NO. The removal efficiency of NO_2 kept above the level of 97% in 3 hrs, while that of NO was around 52.8%~58.1%. Therefore the overall removal efficiency, and thus the final formulation of the absorbent should be determined by the adsorb ability for NO. The finally selected formulation named JA is: $Ca(OH)_2$: zeilite =

50% : 50% (weight ratio) based on eqn. (1). Substitute x_1=50, x_2=50 into the regression eqn. (2), a predicted absorption value in 3 hrs for NO_2 can be acquired at 281.8mg. The adsorbent JA was prepared using the optimized formulation, and its real absorb abilities were determined with the same method, the results showed that the absorption quantities of JA in 3 hrs were 156.7mg for NO, and 289.9mg for NO_2, which were close to the predicted values, proving a high significance of the regressions, and an acceptable reliability of the equations.

3.3 Comparisons between JA and active carbon

The adsorb ability of active carbon was also tested in the same condition. The results showed that the NO_x adsorption quantity of active carbon in 3 hrs was 166.2mg, which was 57.3% of the absorption quantity of JA. Furthermore, the concentration of the outlet NO was measured higher than the inlet concentration. Besides, there was also CO concentration detected in the outlet gas. Therefore, it can be deduced that NO_2 was reduced to NO at the surface of active carbon.

3.4 Breakthrough curve and saturated adsorption capacity of JA

JA was tested with the system (shown in Figure 1) continuously until it was totally broken through. The saturated adsorption quantity was also calculated. The breakthrough curve is shown in Figure 3.

13.0750g of JA was used in the testing. The removal quantity of NO was measured 654mg and that of NO_2 was 2249mg. It can be calculated that the adsorption capacity was 5.0% for NO, 17.2% for NO_2, thus 22.2% for NO_x in the condition.

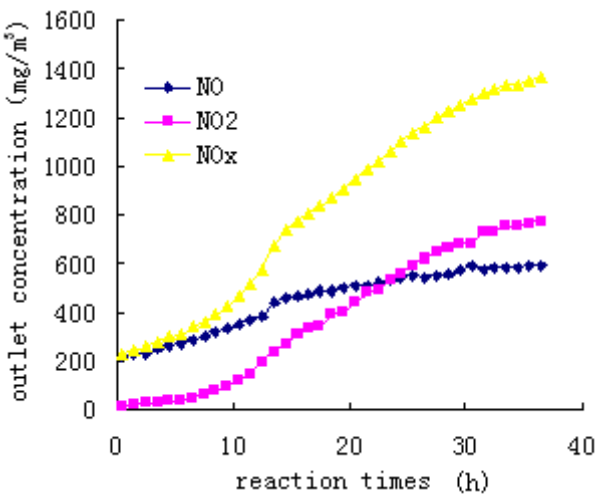

Figure 3: Breakthrough curve of JA.

3.5 Comparisons between uniform design and orthogonal design [5]

Compared with the traditional orthogonal design, the uniform design has the following advantages:

(1) The ingredient percentages in orthogonal design can not be taken as the levels of the factors because it would result in the summations not equal to 1.
(2) In uniform design, only one experiment is needed for each level of the factors, thus the experiment number is equal to the level number. As for orthogonal design, experiment number equals the square of level number.
(3) The levels of the factors in uniform design can be adjusted to avoid the reactants of top grade meeting with reactants of low grade, thus to prevent too violent or too slow reactions.

4 Conclusions

(1) Three kinds of natural minerals and slaked lime were introduced in the research. Uniform design was used in the experiments to develop a kind of NO_x adsorbent. The best formulation has been acquired basing on the designed 12 experiments.
(2) In the experiment condition, the acquired best formulation of the absorbent is 1:1 (weight ratio) for $Ca(OH)_2$ and zeolite. Results showed that the absorbent JA can adsorb 156.7mg of NO and 289.9mg of NO_2 simultaneously in 3 hrs in the experiment condition, while the saturated adsorption quantity of NO_x is 22.2%.

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Effects of process changes on concentrations of individual malodorous sulphur compounds in ambient air near a Kraft pulp plant in Thunder Bay, Ontario, Canada

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Abstract

Ambient air samples were collected at several locations in the community around a major Canadian pulp and paper plant over a period of several months, before and after major process changes. These changes, which occurred in the spring of 2006, included the closure of one of two Kraft pulp mills on site and the shutting down of a chemical recovery boiler and associated black liquor oxidation systems. The facility currently operates one Kraft mill producing both hardwood and softwood market pulp and a two machine paper mill with thermomechanical and deinking pulp mills. All ambient air samples were collected downwind from the plant in Teflon bags and analyzed for volatile reduced sulphur compounds using a gas chromatograph equipped with a pulsed flame photometric detector and a cryogenic trapping system. The frequency distributions of the concentrations of hydrogen sulphide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulphide (DMS), and dimethyl disulphide (DMDS) were compared before and after the process changes. DMS was found to be the most abundant reduced sulphur compound in ambient air before the changes with an average concentration of 1.49 ppbv. After the changes, the average concentrations of CH_3SH, DMS, and DMDS decreased by 28, 70, and 58%, respectively. The concentration of H_2S was below its detection limit of 0.90 ppbv in most of the samples collected both before and after the process changes.
Keywords: reduced sulphur compounds, Kraft pulp mill, odour, pulsed flame photometric detector, gas chromatography, cryogenic trap, hydrogen sulphide, methyl mercaptan, dimethyl sulphide, dimethyl disulphide.

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1 Introduction

The Bowater plant located in Thunder Bay, Ontario, Canada includes both newsprint and Kraft pulp manufacturing facilities. Before 3 May 2006, two Kraft pulp mills ("A" mill and "B" mill) produced a combination of hardwood and softwood elemental chlorine free bleached market pulp. The chemical recovery process utilized two recovery boilers ("B" and "C") and two lime kilns ("A" and "B"). On 3 May 2006, the "A" Kraft mill, which included the "B" recovery boiler and the "A" lime kiln, was shut down.

Since 1994, the plant has invested in several air improvement initiatives to reduce total reduced sulphur (TRS) and particulate emissions, including:

i. installation of scrubbers and electrostatic precipitators on the bark boilers (1994/1996),
ii. improvements to the "B" Recovery Boiler (1995/99/02),
iii. upgrades to the bleach and chemical plant scrubbers (2001/03),
iv. removal of the old "A" recovery boiler (2001),
v. construction of new low odour "C" recovery boiler utilizing 3 levels of combustion air to ensure complete combustion of the black liquor and a non-contact evaporation system to evaporate water from the liquor prior to burning (2001),
vi. discontinuation of weak black liquor oxidation system (2003) and replacement with a total heat recovery (THR) system where pure oxygen is used to more efficiently converting the sulfide in black liquor to thiosulfate and thus raise the heating value of the black liquor prior to burning in the recovery boiler,
vii. replacement of wet scrubbers on the "A" and "B" lime kilns with electrostatic precipitators (2004), and
viii. installation of a dilute non-condensable gas (DNCG) system to collect, concentrate, and incinerate reduced sulfur gases emitted from roof top tank vents and chip bin exhausts (2004).

Four reduced sulfur compounds, i.e. hydrogen sulfide (H_2S), methyl mercaptan (CH_3SH), dimethyl sulfide (DMS), and dimethyl disulfide (DMDS) emitted from kraft pulp mills are mainly responsible for odour problems. These compounds are collectively designated as Total Reduced Sulphur (TRS). The odour threshold for TRS compounds are very low: 0.41 ppbv for H_2S, 0.07 ppbv for CH_3SH, 3.0 ppbv for DMS, and 2.2 ppbv for DMDS, where ppbv refers to parts per billion on a volume basis [1].

The TRS concentration is defined as the sum of the sulphur contributions from the four individual TRS compounds:

$$C_{TRS} = C_{H_2S} + C_{CH_3SH} + C_{DMS} + 2\,C_{DMDS} \tag{1}$$

where C refers to concentration on a volume or molar basis. Under the ambient air quality criteria (AAQC) in Ontario, the limit on 1-hour average TRS concentration is 40 mg/m^3 as H_2S [2], which corresponds to a TRS volume concentration of 27 ppbv. TRS compounds normally present no health hazard to humans, except at very high concentrations.

The determination of reduced sulphur compounds is complicated by their high reactivity, which can result in severe losses during sampling and analysis. The materials that come in contact with the samples must be inert toward sulphur compounds to minimize these losses.

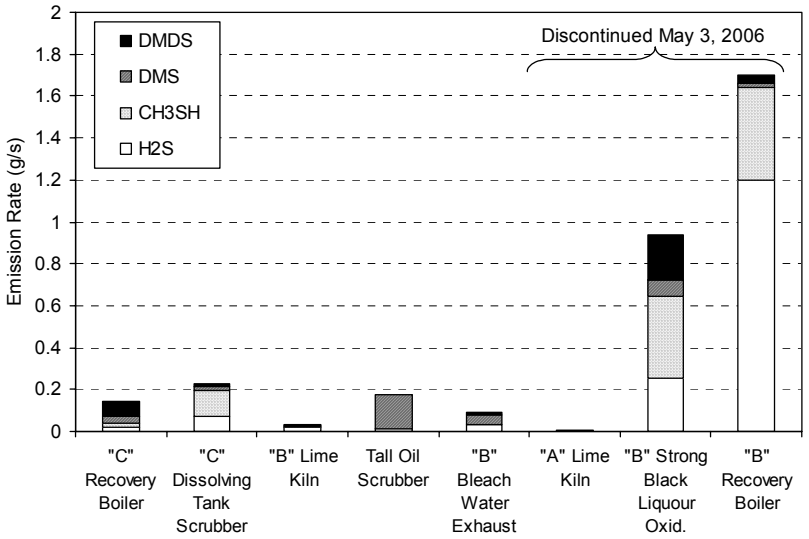

Figure 1: Summary of main TRS sources for Bowater facilities [3].

Table 1: Annual emissions of TRS compounds for the entire Bowater plant.

	H_2S	CH_3SH	DMS	DMDS
Emissions (kg/yr)				
- Before 3 May 2006	47,939	29,478	6,262	10,999
- After 3 May 2006	4,351	4,422	3,359	3,039
Percent Reduction	91%	85 %	46%	72%

1.1 TRS emissions inventory

Figure 1 shows the emission rates of TRS compounds in g/s from the major individual point sources at the Bowater plant measured in September 2005 [3]. All sources operate between 94 and 98% of the time, except for the tall oil scrubber, which only emits 8% of the time. The “B” Recovery Boiler and the B Strong Black Liquor oxidation unit were by far the largest sources of TRS compounds before 3 May 2006. However, these sources were discontinued with

the shut-down of the "A" Kraft mill on 3 May 2006. Annual emissions of TRS compounds in kg/year for the entire plant before and after 3 May 2006 are reported in Table 1. The operating times of each source were taken into account to calculate annual emissions. The emissions of H_2S and CH_3SH were the most affected by the closure of the "A" Kraft mill, with reductions of 90.9% and 85%, respectively. Emissions of DMS and DMDS were also reduced by 46.4 and 72.4%, respectively.

1.2 Objectives

This paper reports the results of analysis of TRS compounds in ambient air samples collected before and after 3 May 2006 downwind of the plant main stack. The effects of the "A" Kraft mill shutdown on the concentrations of individual TRS compounds in ambient air are quantified. The changes in ambient air concentrations are then compared with changes in TRS emission rates from the plant.

2 Methods

2.1 Air sampling methods

Ambient air samples were collected in the community surrounding the Bowater plant outside the plant boundaries from 5 April to 14 September 2006. Before the shutdown of the "A" Kraft mill, a total of 18 samples were collected on 9 different days between 5 April and 2 May 2006. After the shutdown of the "A" Kraft mill, 39 samples were collected on 21 different days between 23 May and 14 September 2006. On each sampling date, the sampling location was selected to be downwind from the plant main stack. All the sampling was done within a 2-km radius from the plant. Figure 2 shows a map of the 10 sampling locations that were used around the Bowater plant.

A schematic of the air sampling apparatus is shown in Figure 3. Ambient air is drawn through a 1/4-in OD Teflon sampling tube whose inlet is held at 2 m above the ground by pole mounted on a tripod. The Teflon tube is connected to one side of a Teflon port inserted through the wall of a 1450 Pelican case (Pelican Products, Torrance, California) having interior dimensions of 37.1 x 25.8 x 15.2 cm. The other side of the Teflon port is connected to a 2 L (23 cm x 23 cm) Teflon bag (Chromatographic Specialties, Brockville, Ontario) held inside the Pelican case. A second port on the Pelican case allows for connection to an SKC 224-44XR air-sampling pump (SKC Inc., Eighty Four, Pennsylvania) via Tygon tubing. Because the Pelican case is airtight, drawing air from the interior of the pelican case with the air sampling pump causes the Teflon bag to fill with ambient air drawn through the Teflon sampling tube. This set-up ensures that the sampled air only comes in contact with Teflon, which is inert towards reduced sulphur compounds. Each air sample was collected within a period of 4 min at a rate of 450 mL/min.

Figure 2: Aerial photograph of the Bowater plant and sampling locations.

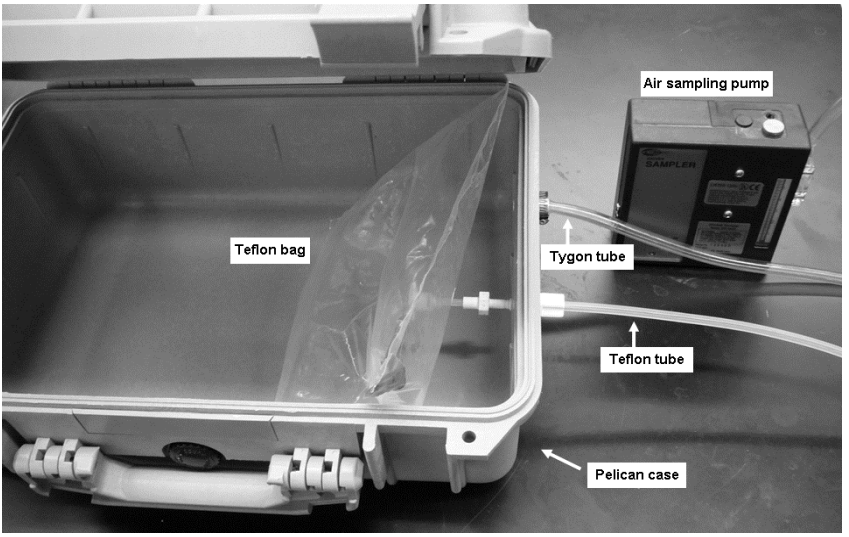

Figure 3: Schematic of air sampling apparatus.

During sampling, a portable meteorological station (Signal Weather Services, Dryden, Ontario) was used to monitor the wind speed, wind direction, temperature, and relative humidity at 1-minute intervals. Once an ambient air sample is collected, the Pelican case is opened, the valve of the Teflon sampling bag is closed, the bag is removed, and a new bag is installed for collecting the next air sample. After collection, the air samples were stored in an insulated cooler bag with cold packs for transportation to the laboratory. Upon arrival in the laboratory, the samples were transferred to a fridge and analyzed within 2 to 3 hours after collection. To minimize sampling costs, Teflon bags were re-used after flushing at least three times with ultra-high purity nitrogen gas. Tests were carried out to ensure that re-used bags did not introduce contamination in the new samples.

2.2 Analytical methods

The ambient air samples were analyzed by a trace level sulphur analyzer consisting of a gas chromatograph (Varian CP 3800, Palo Alto, California) equipped with a pulsed flame photometric detector (PFPD) and interfaced with a cryogenic trap (Lotus Consulting, Long Beach, California) for pre-concentration of ambient samples. Air samples were introduced in the Lotus preconcentrator by connecting the valve of the Teflon bag to the inlet port of the preconcentrator with a Teflon fitting. A mass flow controller located downstream of the cryogenic trap controlled the flow rate at which air was removed from the bag. For each analysis, a total volume of 210 mL of ambient air flowed through the trap. All the tubing that comes into contact with the air sample in the analytical equipment is treated with a silcosteel™ coating (Restek Corporation, Bellefonte, Pennsylvania) to prevent adsorption of active sulphur compounds. Details of the analytical system and calibration procedures can be found in Catalan [4]. The calibration was repeated every two weeks to ensure accuracy of the analytical results. The absolute instrument sensitivity (AIS) was determined to be 0.90 ppbv for H_2S, 0.51 ppbv for CH_3SH, 0.092 ppbv for DMS, and 0.009 ppbv for DMDS. The AIS is a reliable and conservative measure of detection limit for volatile sulphur compounds by GC-PFPD [5].

The stability of reduced sulphur compounds in the Teflon sampling bags was assessed by introducing a gas mixture containing 2.1 ppbv H_2S, 4.7 ppbv CH_3SH, 1.5 ppbv DMS, and 1.0 ppbv DMDS in a clean Teflon bag and then periodically withdrawing aliquots which were analyzed to monitor the changes in concentration with time. These initial concentrations were representative of concentrations measured in actual ambient air samples. Figure 4 shows the composition of the gas mixture as a function of time. Any change from the initial concentration is due to decomposition of TRS compounds in the gas phase or adsorption on the bag walls. The concentrations of all the TRS compounds remained within 10% of the initial concentrations for at least 3 hours after the Teflon bag was filled. CH_3SH exhibited the largest losses (-7% after 2.7 hours and -20% after 3.8 hours). By contrast, the concentration of DMDS was found to remain constant for more than 7 hours. Similar results were obtained when the initial concentrations were doubled. These results indicate that no significant

losses of TRS compounds from ambient air samples can be expected during the time that separated sample collection from analysis (< 3 hours).

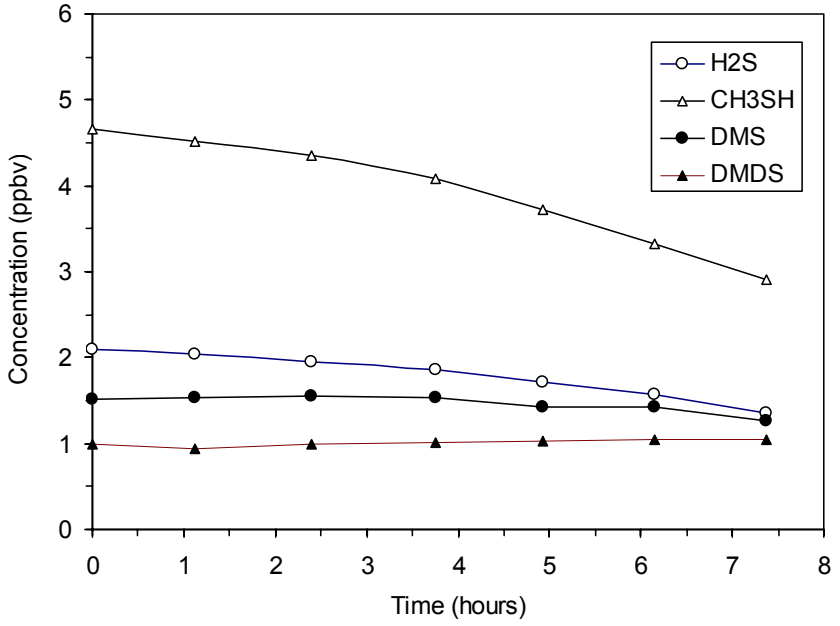

Figure 4: Stability of TRS compounds in Teflon sampling bag.

3 Results and discussion

Figures 5(a)–(d) show the frequency distributions of the concentrations of DMDS, DMS, CH_3SH, and H_2S, respectively. For each compound, two distributions corresponding to the data taken respectively before and after 3 May 2006 are shown. The *x*-axis represents the frequency of ambient air samples having a concentration greater than the stated values. For example, Figure 5(b) shows that 59% of the samples collected before 3 May 2006 had a DMS concentration greater than 1 ppbv, whereas only 12% of the samples collected after that date had a DMS concentration greater than 1 ppbv. Frequency distributions for DMS and DMDS concentrations consistently shifted toward lower concentrations after 3 May 2006 (Figures 5(a) and 5(b)), thus demonstrating the beneficial effect of the "A" Kraft mill shutdown on concentrations of DMS and DMDS in ambient air.

The frequency distributions for CH_3SH concentrations (Figure 5(c)) contain much fewer data points than those for DMS and DMDS. This is because CH_3SH was below the detection limit in most of the ambient air samples. Before 3 May 2006, CH_3SH was detected in only 35% of the samples. After that date, CH_3SH was detected in only one sample out of 39 samples. On the single occasion when

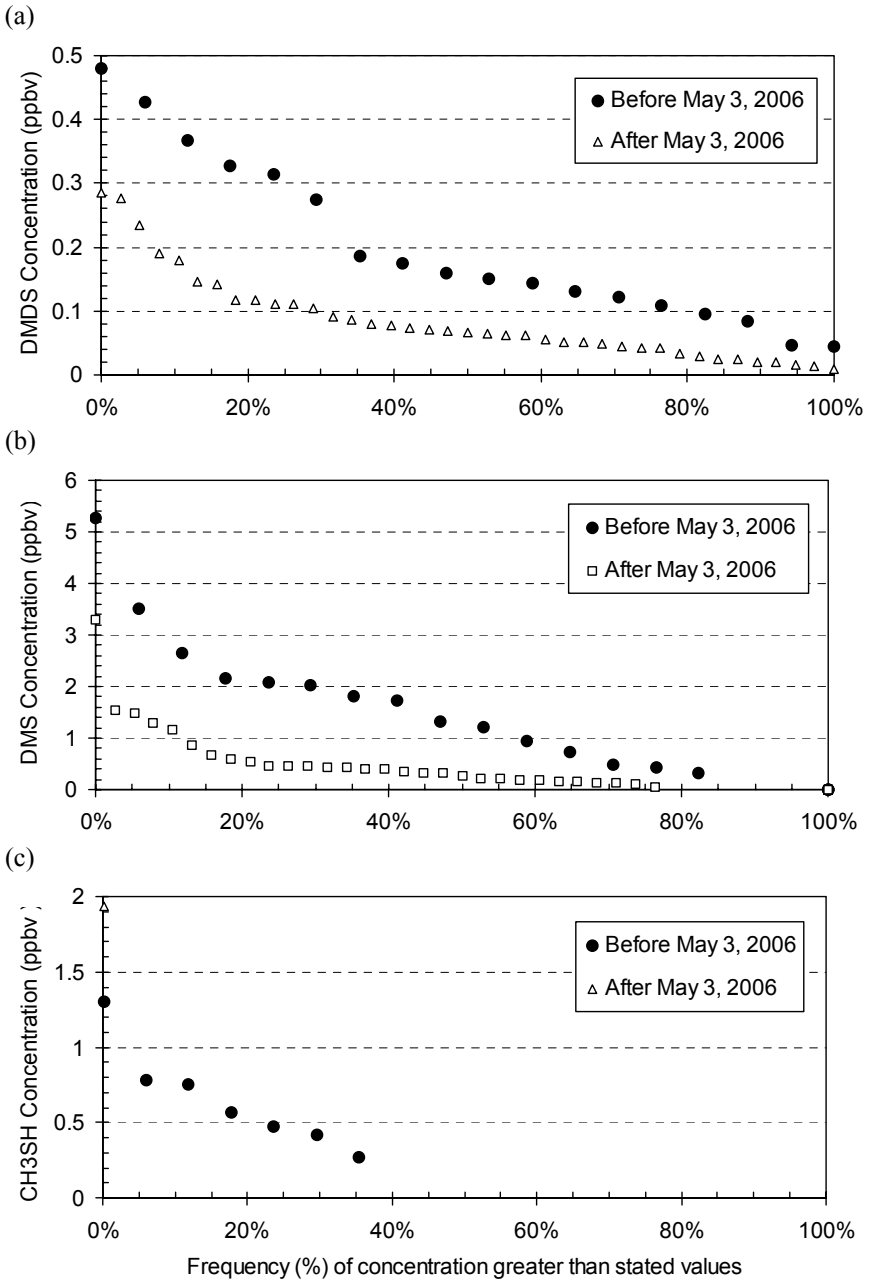

Figure 5: Frequency distributions of (a) DMDS, (b) DMS and (c) CH_3SH concentrations in ambient air samples.

(d)

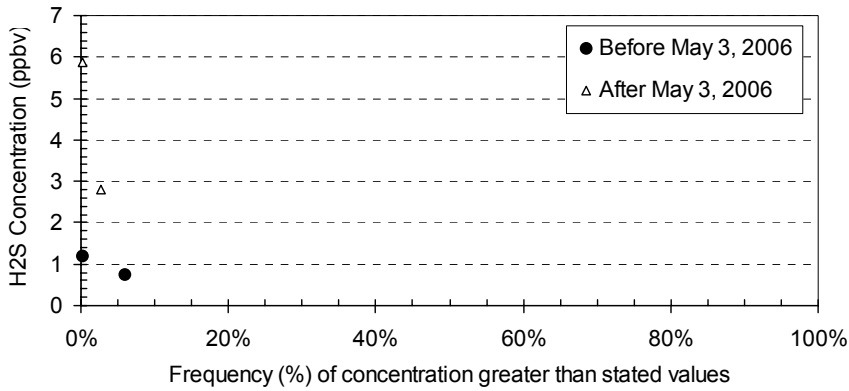

Figure 5 (cont'd): Frequency distributions of (d) H_2S concentrations in ambient air samples.

CH_3SH was detected (30 August at 2:21pm), its concentration was the highest that was recorded in the entire sampling campaign (1.94 ppbv). Overall, the "A" Kraft mill shutdown resulted in a large decrease in the frequency of detectable CH_3SH concentrations in ambient air samples. It is worth noting that on three occasions before 3 May 2006, CH_3SH was detected and quantified at levels below the reported absolute instrument sensitivity of 0.51 ppbv. This is because the AIS is calculated using an average root mean square (rms) noise evaluated over several chromatograms [5], whereas the actual rms noise for a particular chromatogram can be lower than the average rms noise, thus allowing measurement of the analyte below the reported AIS.

The frequency distributions for H_2S concentrations indicate that H_2S was only detected in two samples before and after 3 May 2006 (Figure 5(d)). On the two occasions when H_2S was detected after 3 May 2006, the H_2S concentrations (2.8 and 5.9 ppbv on 20 June at 3:52pm and 30 August at 2:21pm, respectively) were higher than concentrations detected before 3 May 2006. Therefore, the data for H_2S do not reveal a beneficial effect of the "A" Kraft mill shutdown on H_2S concentrations in ambient air. However, because more than 90% of the samples had undetectable H_2S concentrations, both before and after 3 May 2006, no reliable conclusion can be made about trends in H_2S concentrations.

For each TRS compound, Table 2 presents the average concentration before and after 3 May 2006, the percent change in average concentration resulting from the "A" kraft mill shutdown, and the confidence level that the difference in average concentrations is statistically different, as determined from a Student's *t*-test. Concentrations below the detection limit were arbitrarily assumed to be equal to half the AIS (i.e., 0.45 ppbv for H_2S, 0.25 ppbv for CH_3SH, and 0.046 ppbv for DMS) for the purpose of calculating average concentrations. This assumption greatly affected the average concentrations of H_2S and CH_3SH but had almost no effect on the average DMS and DMDS concentrations because

DMS was rarely below the detection limit and DMDS was always above the detection limit.

Table 2: Average concentrations of TRS compounds in ambient air before and after the shutdown of the "A" Kraft mill.

	H_2S	CH_3SH	DMS	DMDS
Before 3 May 2006	0.51	0.41	1.49	0.202
After 3 May 2006	0.65	0.29	0.45	0.086
Percent of Change	+27%	-28%	-70%	-58%
Confidence level (*t*-test)	62%	83%	99.4%	99.8%

DMS was the most abundant TRS compound before 3 May 2006 with an average concentration of 1.49 ppbv. The average DMS and DMDS concentrations in ambient air dropped respectively by 70% and 58% after the shutdown of the "A" Kraft mill. These drops are comparable to the declines in the emissions of these compounds from the plant (46% for DMS and 72% for DMDS, see Table 1). Moreover, the results of the Student's *t*-test indicate that the shutdown of the "A" Kraft reduced the average concentrations of DMS and DMDS in ambient air with a confidence level larger than 99%. The difference in numerical values between changes in emissions and changes in ambient air concentrations could be due to the fact that emissions fluctuate as a function of time. For example, the tall oil plant, which is a major contributor to DMS emissions (see Figure 1), only runs intermittently. Hence, the DMS concentration measured in ambient air is dependent on whether the tall oil plant is operating at the time of sampling. By contrast, the change in DMS emission rate is calculated on a yearly basis and accounts for the number of operating hours of each source.

The results of the Student's *t*-test for CH_3SH indicate that the average concentration of this compound decreased after the shutdown of the "A" Kraft mill with a confidence level of 83%. The average concentration of CH_3SH decreased by 28%, which is much less than the 85% decrease in CH_3SH emissions from the plant (Table 1). However, because CH_3SH was below the detection limit of 0.51 ppbv in most of the ambient air samples collected after 3 May 2006, the actual decrease of the average CH_3SH concentration may be underestimated. For example, if samples with undetectable CH_3SH were assumed to contain no CH_3SH rather than a concentration equal to half the AIS, the calculated reduction in the average CH_3SH concentration would be 80%, which is very close to the change in CH_3SH emissions.

At first glance, the data for H_2S appears to indicate that the average concentration of this compound increased after the shutdown of the "A" kraft mill. However, the *t*-test shows that this would not be a valid conclusion since the confidence level for a change in the average H_2S concentration is only 62%. This low confidence level reflects the fact that most of the H_2S concentrations were below the detection limit of 0.90 ppbv both before and after 3 May 2006.

It is important to point out that the data do not rule out that the average H_2S concentration may have actually decreased after the shutdown of the "A" kraft mill (as could be logically expected given that the H_2S emissions from the Bowater Plant decreased by 91%), but the detection limit for H_2S is too high to demonstrate this effect.

4 Conclusions

On 3 May 2006, the Bowater pulp and paper plant located in Thunder Bay shut down one of its two Kraft mills, thus reducing its overall air emissions of H_2S, CH_3SH, DMS, and DMDS by 91, 85, 46, and 72%, respectively. Analyses of ambient air samples collected in the community surrounding the plant between 5 April and 14 September 2006 have shown that the concentrations of CH_3SH, DMS, and DMDS decreased by 28, 70, and 58%, respectively after the shutdown date. The effect of the shutdown on H_2S concentrations in ambient air could not be ascertained because most of the samples had H_2S concentrations below the detection limit of 0.90 ppbv, both before and after the shutdown.

Acknowledgement

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Odour studies and health risk assessment: two complementary approaches in response to residents' complaints

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Abstract

In this paper we present an approach to assess odour impact is based on odour measurements and air dispersion modelling. This approach makes it possible to estimate the frequency of odour perception and nuisance in the near vicinity of industrial, agricultural or municipal facilities.

A health risk assessment, based on toxicological reference values (TRVs), is also presented in order to consider the toxicity of odorous molecules in impact studies (chronic exposure of the population).

This paper reports the joint and complementary characteristics of these two approaches.
Keywords: odour, impact, health, risk, assessment, modelling, toxicity, olfactive, complaints, olfactometer.

1 Introduction

Concern over the toxicity of odours emitted by industrial sites are often put forward by local residents. In general, the population thinks that bad odours are toxic, which is not necessarily true. For example, hydrogen sulphide can be beneficial as a thermal cure but may be toxic if perceived between 10 and 250 ppm, and even deadly at concentrations beyond 500 ppm (short exposure to concentrations between 500 and 1,500 ppm leads to respiratory paralysis and death) [1]. Carbon monoxide however is odourless but deadly beyond 800 ppm [2].

In reply to these concerns, two approaches may be developed: first, the odour problem (type, source, impact of odours on resident populations and solutions to reduce olfactive emissions) and second, the toxicity aspect of these odorous

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molecules (hazard identification, quantification of exposure levels, risk assessment) [3]. The methods and problems covered by these two approaches, developed in four stages, are complementary and joint.

2 Characterization of the site

Standardized olfactometric measurements are required on the odorous sources when a facility has an impact on the air quality and causes citizen complaints. Odorous air samples are sent to an odour laboratory to determine the odour concentration of each of the odorous sources as well as the odour emission rate in order to establish their hierarchy and to determine their contribution to the overall odours at the site.

A physico-chemical diagnosis is conducted for all the on-site emissions in order to identify the principal molecules emitted into the atmosphere. The type, flow, data on toxicological effects on humans of each chemical compound determine the risk tracer compounds selected to assess the human health risks. Furthermore, an environmental study of the site is carried out to identify its surrounding socio-economic context (other industries, census of populations and their residence area, rural or urban area, etc.).

3 Hazards identification and dose-response ratio

The ratio between the exposure level to odours and pollutants and the incidence and gravity of these effects is estimated. For odorous molecules, the main route of exposure is through inhalation.

In France, regulatory emission values have been issued concerning the odour output allowed, based on the height of the emissions for classified facilities for the protection of the environment (IPCE), "beyond which discomfort may be felt in the surrounding area" (Decree of February 2, 1998, Article 29 and its Application Circular of December 17, 1998). In particular, for the treatment of cadavers, wastes or by-products of animal origin (Decree of February 12, 2003), "the odour output must comply with the following air quality objectives: the odour concentration calculated within a radius of 3 km from the property limits of the site must not exceed 5 ou_E/m^3 for more than 175 hours per year for an existing facility" [4]. These reference values for odour concentrations and the associated olfactive discomfort are based on both the source and the environment.

The French law on air (December 30, 1996) and its decrees (May 6, 1998 and February 15, 2002) recommends that "the air we breathe must not be harmful to our health" and defines the environmental values for chemical pollutants (air quality objectives).

Chemical substances of the odour may have acute effects (due to strong exposure for a short period) and sub-chronic or chronic effects (due to low exposure for a long period). We also differentiate pollutants with threshold effects (there is a level of exposure below which there is no risk) and pollutants without a threshold (any amount of exposure carries with it a degree of risk).

For each selected pollutant, the intrinsic effects on human health, particularly through inhalation, is examined. The Toxicological Reference Values (TRVs) available in toxicological databases (WHO, US EPA, ATSDR, etc.), specific to each pollutant, serve as a reference for exposure limits for populations living around the facility. These TRVs, based on an epidemiological study or animal experiments, are established for a specific duration for a given route of exposure.

4 Exposure assessment

The assessment of the exposure of populations may be conducted for odours and for pollutants through an air dispersion modelling. This method allows a determination of foreseeable environmental concentrations of odours or pollutants, their area of impact and establishes the frequency in which the threshold value is exceeded. An example of this map is given in Figure 1 for exposure levels to a pollutant (fictitious case).

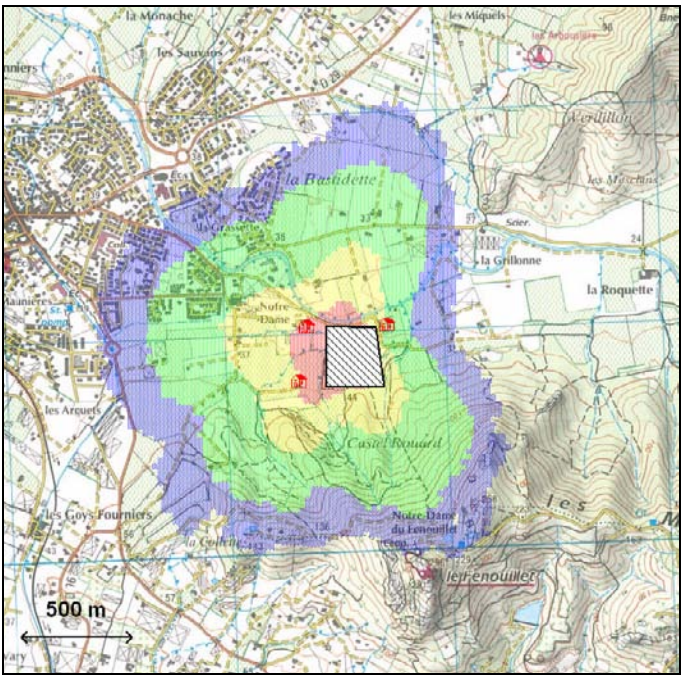

Figure 1: Example of a result from air dispersion modelling.

Furthermore, physico-chemical measurements may be conducted at different points in the environment in order to verify the consistency of results obtained by modelling or to quantify environmental concentrations if the modelling is not adapted.

The impact of odours may also be quantified through the following methods:

- a citizen survey to obtain feedback on the olfactive perception of the residents, the discomfort caused by olfactive nuisances and the main areas affected by these odours;
- an olfactive observation campaign carried out by volunteers trained to recognize odours to provide a qualitative description of odours perceived and the impact differences.

5 Risk characterization

Within the context of odour studies, the odour output at emission and the frequency in which threshold values are exceeded in the environment are compared to the reference values. In addition, the calculation of olfactive comfort indices (stipulated in the French decree of February 12, 2003) allows the drawing up of maps (Figure 2) indicating the different areas with the associated comfort indices (good, average, degraded, poor).

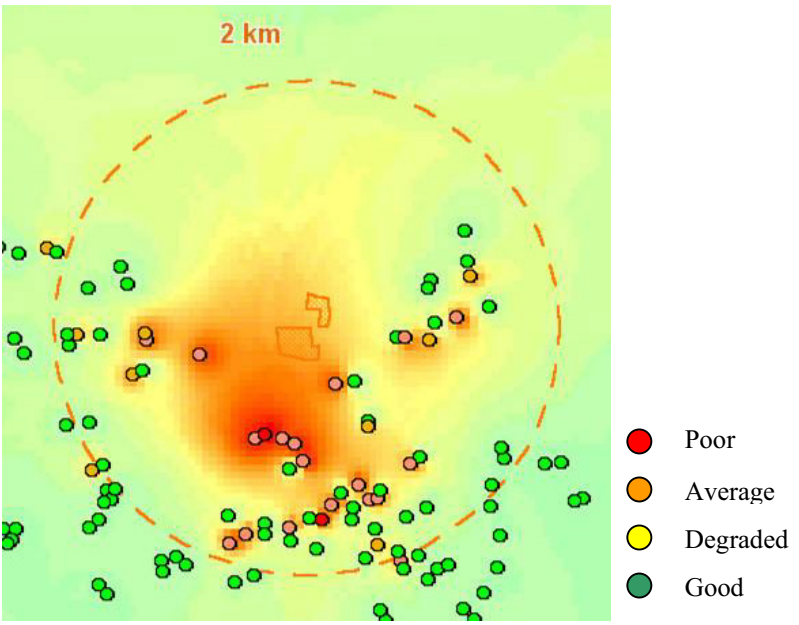

Figure 2: Comfort indices for populations living near a facility.

Within the context of the health risk assessments, environmental concentrations of pollutants are compared with the Toxicological Reference Values in order to establish if there is a health risk for the residents.

Based on results obtained, it may be necessary to reduce emissions at the source both for the odours and pollutants.

The odour studies and health risk assessments are two problems which are:

- Complementary, insofar as they cover the olfactive perception, the discomfort aspect and the chemical risk,
- Joint, since odour is a perception resulting from the stimulation of the olfactive system through a more or less complex mixture of chemical molecules which may present different degrees of toxicity.

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Atmospheric volatile organic compounds in a Portuguese mountain region

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Abstract

Ambient air volatile organic compounds (VOCs) samples were simultaneously collected at two sites during two consecutive weeks of June 2006 at Alvão Natural Park, in the north of Portugal, where spring and summer ozone exceedances have been registered over the last years. One of the sites was located at the background air quality monitoring site of Lamas de Olo, in the Alvão Mountain. Other site was sampled on the outskirts of the Park to characterise the predominant upwind air masses associated with higher ozone levels. Stainless steel canister and sorbent tube sampling was performed for the determination of C_2-C_6 and C_6-C_{11} non-methane hydrocarbons, respectively, after analysis by gas chromatography coupled with flame ionisation detection or mass spectrometry.
Keywords: VOCs, tropospheric ozone, rural area, PEC.

1 Introduction

In the last years, several photochemical episodes have occurred both in urban and suburban sites [1, 2] as well in rural areas [3, 4], being related to a set of photochemical reactions between VOCs and NO_x. Tropospheric ozone is a photochemical secondary pollutant of major importance with effects on health, agriculture productivity, natural ecosystems and materials [5-7].

In the past, air quality problems in Portugal were usually focused on urban or important industrial areas, placed mainly along the Atlantic coast. Nevertheless, some studies performed in the last decade showed elevated ozone levels in rural areas far from the anthropogenic source emissions [8-10].

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High temperature and strong radiation during warm and hot seasons are characteristics that favour photochemical formation of secondary pollutants, such as ozone, in the Portuguese territory. Since the start-up of Lamas de Olo, a rural air quality monitoring station, at an altitude of 950 m a.s.l., in the Natural Park of Alvão (NPA), the number of ozone exceedences registered in Portugal has increased significantly [11]. In the last five years, the highest ozone levels in Portugal were recorded in this air quality station. This place reached the highest hourly average level in Europe in 2005, with 361μg.m^{-3} [11]. To explain these high values, it will be crucial to evaluate the concentrations of ozone precursor, like NO_x and VOCs. In rural areas, biogenic VOCs play an important role in photochemical chemistry affecting ozone production.

Aiming to understand the high levels of ozone in this area, several samplings were performed during last summer (2006) to characterise and quantify the VOCs composition and trying to identify their possible contribution for ozone production.

2 Experimental

In the period of 23rd June to 1st July 2006 an air quality monitoring field campaign was performed in NPA in the NE of Portugal at two sites (Figure 1), simultaneously. The first location is situated at an elevated of 500 m a.s.l. in the Basal Zone of West region of NPA, close to Ermelo village. The second location is situated in the East upper zone of NPA, in Lamas de Olo, coincident with the air quality station of the national network.

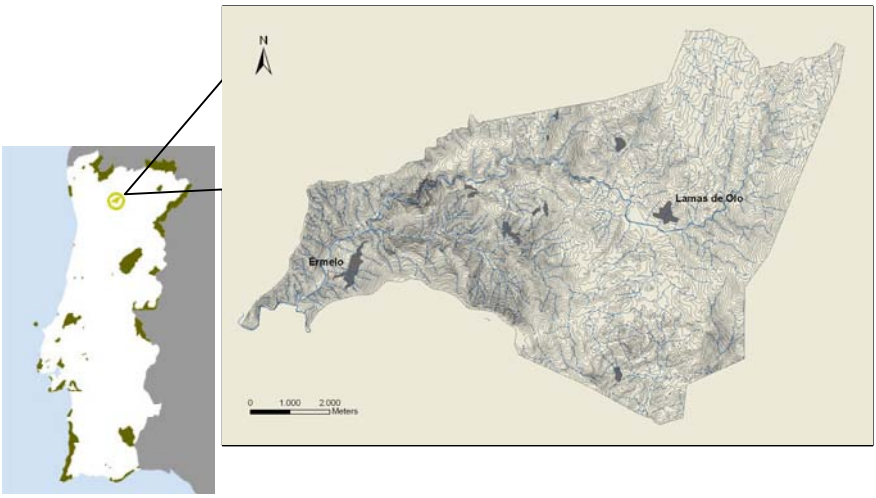

Figure 1: Maps of Portugal and NPA area, where the sampling sites are marked (map of Portugal from www.icn.pt) [12].

The upper zone is dominated by large granite blocks, makes the landscape harsh and angular. The Basal Zone, with its narrow enclosed valleys is characterised by schist and by the presence of an abrupt change of altitude. This region benefits from the joint effect of the temperate Mediterranean type climate and the alpine influences (caused by the altitude). The NPA include a large floristic diversity which main species are: *Quercus pyrenaica*, *Quercus robur*, *Bétula alba* and small patch of *Quercus suber*. The rocky upper zone is dominated by *Erica sp*., *Cytisus striatus*, *Baccharis trimera*, *Cistus salvifolius* and *Ulex parviflorus*.

At each location ozone and NO_x concentrations were monitored continuously with Environment-O_3 model 41M and Environment AC model 42C, respectively. Meteorological parameters were measured with portable meteorological stations equipped with standard sensors. Low VOCs (C_2-C_7) were sampling using stainless steel canister. Air samples were analysed by GC-FID, Chrompack® CP 9001, equipped with a specific cryogenic pre-concentration system [13]. The GC-FID analytical conditions were adapted from *J&W Technical Support - Ozone Precursor Analysis on GS-Alumina/KCl* (http://www.jandw.com).

The heavy VOCs (C_5-C_{11}) were collected in a stainless steel tube trap, filled with 120 mg of Tenax-TA (60-80 mesh) and 100 mg of Carbotrap B (60-80 mesh). The samples were desorbed and analysed by thermal desorption - cryogenic concentration method using a GC-FID, Chrompack® CP 9000, equipped with a Chrompack Thermal desorption-Cold Trap injection (TCT) [10].

3 Results

The temporal variation of the meteorological parameters measured during the sampling campaign at Ermelo and Lamas de Olo is shown in Figure 2.

Highest levels and daily temperature amplitudes were registered at Ermelo. It was also observed that 30th June and 1st July were the hottest days of the sampling campaign. The wind blew predominantly from E, NE and SE in Ermelo, where its speed did not exceed 2 m s $^{-1}$ during daytime, decaying to values close to zero at night. In Lamas de Olo the leading wind directions were from W and N with much higher speeds than in Ermelo, especially in the late afternoon and early night. The altitude, low surface roughness and a poor vegetation land cover may explain the stronger winds registered in the upper zone.

Figure 3 depicts the variation of concentrations of O_3 and NO_x monitored in the two sampling sites.

The profile of O_3 at the low-altitude site (Ermelo) showed lower values and higher daily amplitudes than those registered at the high-altitude site (Lamas de Olo). The highest ozone levels were registered on 30th June, reaching values of 186 and 223 μg m^{-3} in Ermelo and Lamas de Olo, respectively. Throughout the sampling campaign, relatively high nocturnal levels were registered at these two sites. At the upper zone, nocturnal minima higher than 60 μg m^{-3} were measured, reaching sometimes ~150 μg m^{-3}. These high ozone levels during the night-time may be associated with the low NO_x concentrations observed at both sites due to

the weak O_3 titration by the rapid reaction with NO. Altitudinal differences could also be caused by less vertical mixing. In addition, O_3 intrusions with stratospheric origin and reduced loss processes at greater altitudes may explain this phenomenon [14]. Some studies previously performed in mountainous regions of the EU and USA also refer that surface ozone mixing ratios increase with altitude, showing high nocturnal concentrations [14-16].

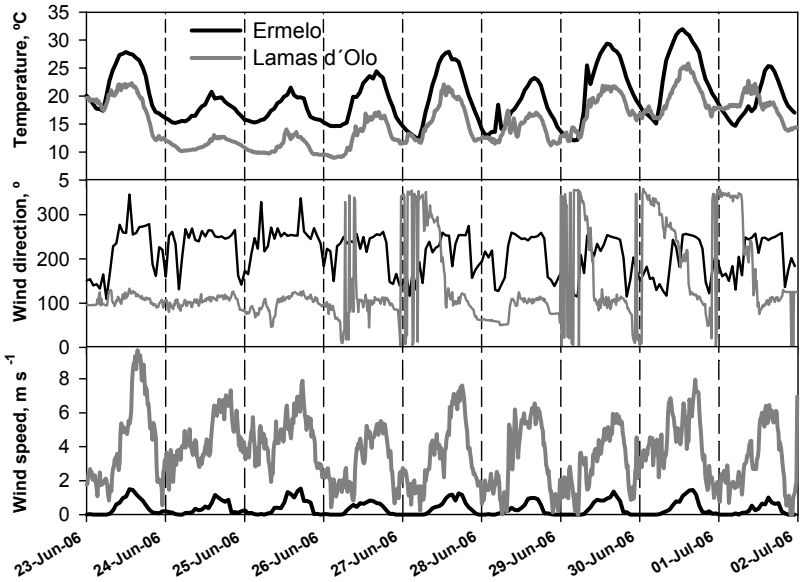

Figure 2: Meteorological parameters from 23rd June and 1st July 2006, at Ermelo and Lamas de Olo.

Throughout the experimental campaign, 30 VOCs were identified whose total concentrations are shown in Figure 4.

In general, the total VOC levels were lower in the upper zone than at the low-altitude site. At Lamas de Olo, the VOC concentrations did not exceed for the whole measuring period, excepting 30th June. Usually, at the basal zone, the C_5-C_{11} VOCs showed higher levels than those of the upper zone. However, on 30th June, the station at greatest altitude registered a huge increase in low VOC concentrations. Since the majority of these compounds present low photochemical reactivity and a long residence time, an increase in their concentrations may reflect the influence of atmospheric transport on a synoptic scale. This hypothesis is confirmed after applying the HYSPLIT (Hydrid Single-Particle Lagrangian Integrated Trajectory Model) model to the upper zone. A dynamic analysis showed that the transport of marine air masses from N and NE of the Iberian Peninsula was prevalent throughout the sampling period. On 30th June, polluted continental air masses coming from the south of Portugal

(backward trajectories at final height of 1000 m) reached the upper zone, whereas air masses (computed at a final height of 500 m) arrived at the north of the Iberian Peninsula after following exclusively an oceanic trajectory. Thus, both stations were affected by different air masses, which may explain the sudden enrichment in low VOCs observed in Lamas de Olo.

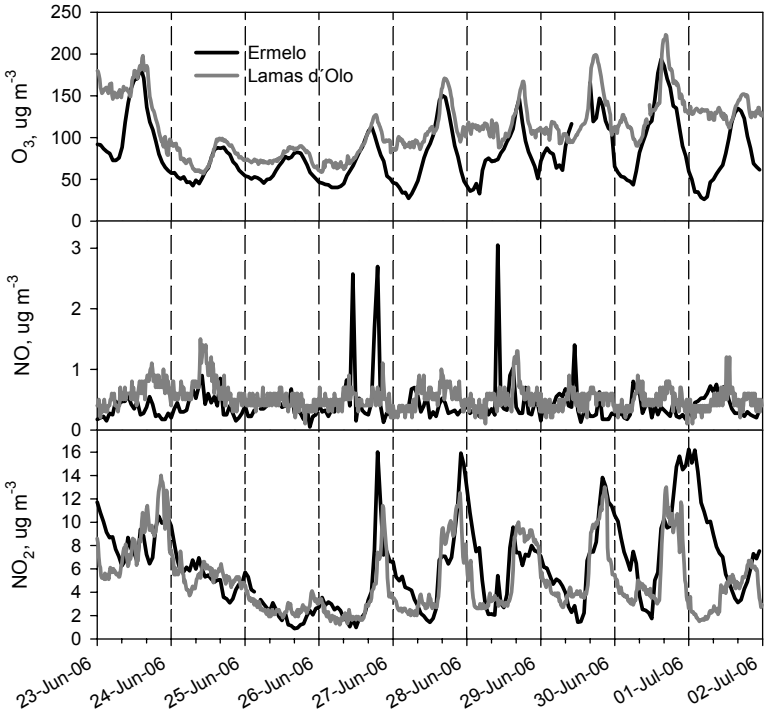

Figure 3: Comparative variation in concentrations of O_3, NO and NO_2 in Ermelo and Lamas de Olo throughout the study period.

In order to evaluate the possible contribution of individual VOCs to the photochemical production of ozone, the Propylene Equivalent Concentration (PEC) was determined [17]. In this calculation, the average concentration of the different low and heavy VOCs measured at both stations, as well the own kinetic constants for the reaction with the OH radical [18, 19] were used.

Figures 5 and 6 depict the average concentrations of low and heavy VOCs and respective PEC. The basal zone is the one with the highest equivalent concentration for both low and heavy VOCs. It was also concluded that compounds of biogenic origin (isoprene and monoterpenes) represented a much higher potential to produce ground ozone than that of other some compounds with higher concentrations.

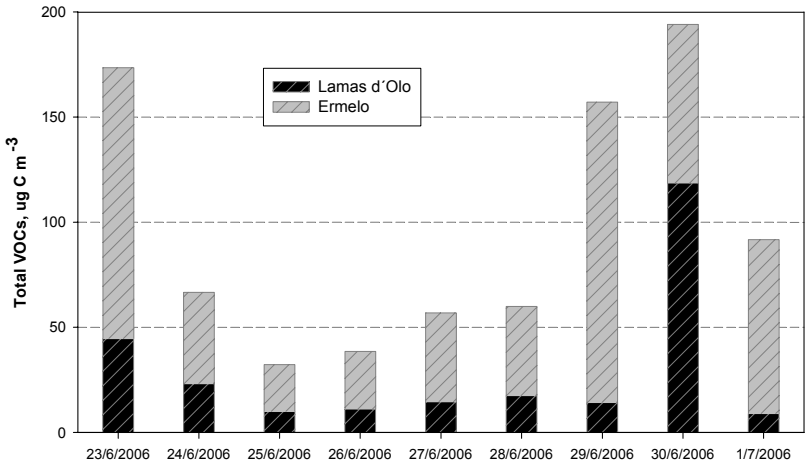

Figure 4: Total VOC concentrations measured in Ermelo and Lamas de Olo.

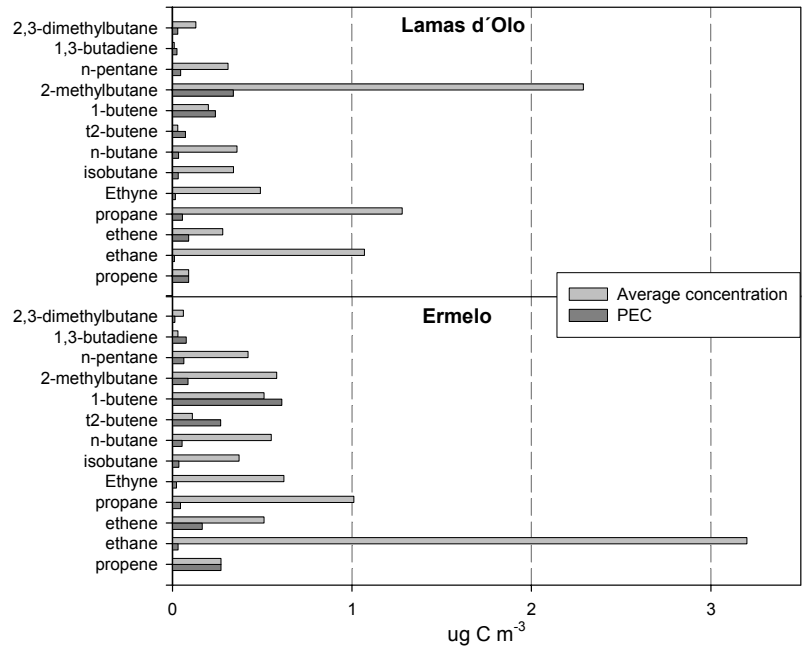

Figure 5: Average concentration and PEC of VOCs, C_2-C_7, between 23rd June and 1st July 2006.

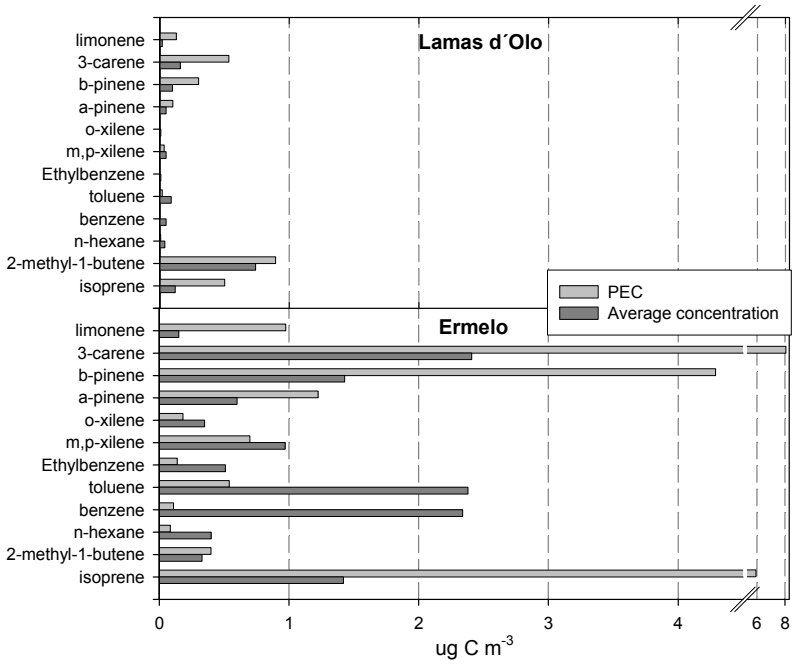

Figure 6: Average concentration and PEC of VOCs, C_5-C_{11}, between 23rd June and 1st July 2006.

4 Conclusions

The upper zone presented higher ozone levels that those registered at the low-altitude site. The low NO_x concentrations observed in both sites may be associated with the weak titration of O_3 by the reaction with NO, directly contributing to the low ozone consumption during the night-time period. In general, the total VOC concentrations were higher at the basal zone. The PEC calculation showed an important contribution of biogenic compounds (*e.g.* 3-carene, isoprene and β-pinene) to the photochemical production of ozone, especially at the basal zone of the natural park. In a near future, this information would be somehow important when developing a photochemical transport model to simulate the ozone formation in this region.

Acknowledgements

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Section 6
Aerosols and particles

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PM and NO_2 at urban sites with different traffic exposure: curb site measurements in Flemish cities

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Abstract

Road transport is known as one of the main sources of urban air pollution, especially PM and NOx. The knowledge that PM may induce adverse health effects is an incentive for progressive cities to evaluate local air quality and to consider what action should be taken. Existing air quality measurement networks measure air pollution at different sites and give an 'average value' for the surrounding area. However, most of these measurement stations are not located at hot spot locations, e.g. close to busy roads. The aim of this study is to assess the air quality at urban (curb site) locations.

PM_{10} daily average values were measured during 3-4 weeks at six locations representing different 'typical' traffic locations: e.g. ring road, access road, parking route, local traffic. NO_2 was measured at all locations.

At the background location lowest concentrations were measured for all parameters. Differences in PM_{10} and NO_2 were observed between the different locations. It seems that NO_2 is more sensitive to traffic exposure than PM_{10}. This is due to the higher background and background variation of PM_{10}. The highest NO and NO_2 values were measured at the bus location,. Highest concentrations of PM_{10} and black carbon are measured at the ring location. However some trends could not be explained.

Keywords: PM, NO_2, urban, traffic, black carbon.

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1 Introduction

Numerous epidemiologic studies have documented adverse health effects of air pollution. Recently, studies have reported associations between residential proximity to busy roads and a variety of adverse respiratory health outcomes in children. Moreover, it was shown that traffic related pollution (PM, NOx and black carbon) is associated with respiratory symptoms in children [1].

The knowledge that PM may induce adverse health effects is an incentive for progressive cities to evaluate local air quality and to looking for actions to be taken. Before cost effective measures can be taken, the actual air quality of the city has to be assessed in order to identify hot spot locations.

Existing air quality measurement networks measure air pollution at different sites and give an 'average value' for the surrounding area. However, most of these measurement stations are not located at hot spot locations, e.g. close to busy roads. In Flanders, the daily average limit value for PM_{10} was exceeded more than 35 times in 17 of 31 monitoring sites in 2005 [2].

Some of the larger Flemish cities have implemented innovative transport and mobility policies in the past decade. Before supplemental cost effective measures can be taken, the actual air quality of the city has to be assessed in order to identify hot spot locations.

The aim of this study is to assess the air quality at urban (curb site) locations.

2 Experimental set-up

2.1 Monitoring sites

The monitoring campaign has been performed in spring (from 15/5 – 18/6) at six sites in the city of Ghent. The selected locations are characterised by different exposure to traffic (see Table 1) e.g. ring road, access road, parking route, local traffic. Traffic counts during morning rush hours (7.30 – 8.30 local time) are displayed in the table for cars and heavy duty (HD) vehicles including buses.

The monitoring sites were selected using emission modelling results, a short screening measurement campaign and information on traffic intensities provided by the local authorities.

The measured concentrations are also compared to data of nearby monitoring stations of the air quality monitoring network.

2.2 Experimental techniques

PM_{10} measurements are performed according to the EU reference method (EN 12341) using a sequential high volume sampler [3].

Filters are analysed with a Smoke Stain Reflectometer to determine black smoke. Particle reflectance of the sampled filters was measured using a reflectometer and transformed into an absorption coefficient according to ISO 9835 [4]. Absorption coefficients were transformed into black smoke concentrations ($\mu g/m^3$) using the method of Roorda-Knaepe et al [5]. Although

black smoke concentrations calculated by this method have a lower accuracy compared to direct EC determination on quartz filters, the method is used here for comparison of different sites.

A mobile emission laboratory is used during one week (at each location) to measure the weekly profile of NO_2 and PM_{10}. NO and NO_2 are measured using a NO/NOx chemiluminescence analyser. PM_{10} profile is measured with TEOM-FDMS which is provided with an aethalometer module for the measurement of black carbon.

Diffusive samplers were used to measure weekly/monthly average NO_2 concentrations.

Table 1: Description of monitoring sites.

Site	Description	traffic counts during morning rush hours (7.30 – 8.30)	
		nr of cars	nr of HD
G1	**background** quiet residential area with only local traffic	40	3
G2	**ring road** ring road location in the north of Ghent with a lot of car traffic and heavy traffic	3180	292
G3	**street canyon – access road** one-way traffic in the city centre in a street canyon	257 **(1)**	28 **(1)**
G4	**parking route – access road** this location is part of a signposted parking route for incoming traffic	**(2)**	**(2)**
G5	**busy city traffic – at waterside** location characterised by busy city traffic next to a waterway	386	18
G6	**bus traffic** location next to the railway station with a lot of bus traffic	**(3)**	**(3)** nr of buses: 508 - 1010

(1) data given are values for evening rush hours**.**
(2) no data available. During morning rush hours traffic-jams are formed.
(3) no data available. Nr. of buses: between 508 (Sunday) - 1010 (schooldays)**.**

3 Results and discussion

3.1 PM_{10} concentrations

The figure below shows the PM_{10} concentrations at all locations and at two nearby stations of the air quality monitoring network. One of them is an urban

station located in the city of Ghent (referred to as 44R701) the other is an urban background station (referred to as 44R710) situated at the east of Ghent.

At location G1 the lowest concentrations were measured. This location is a quiet residential area with almost no traffic and was chosen at the start of the study as background location.

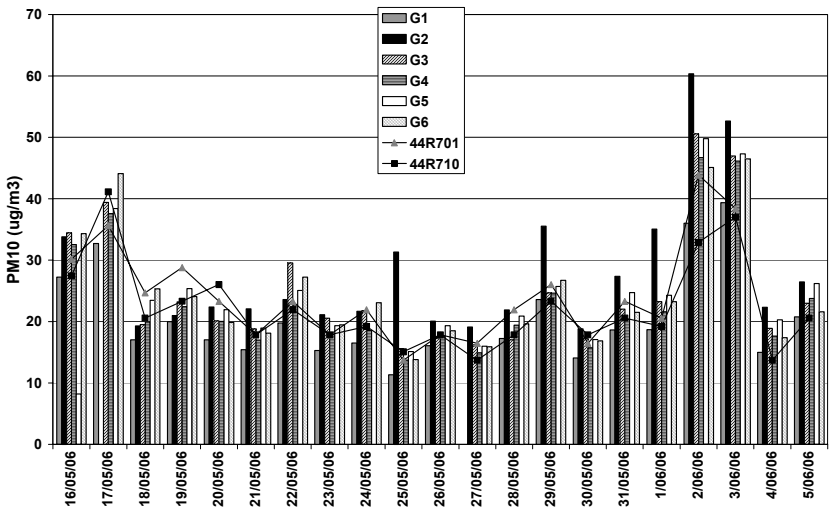

Figure 1: Daily average PM_{10} concentrations ($\mu g/m^3$) measured at six locations in Ghent (G1–G6) and 2 stations of the air quality monitoring network (44R701 and 44R710).

The difference in PM_{10} concentrations compared to the background location is shown in Figure 2. This gives an idea of the contribution of local sources such as traffic. A summary of the distribution of daily average PM_{10} concentrations for different locations is given in Figure 3. The average difference is 8 $\mu g/m^3$ at G2 and 3–5 $\mu g/m^3$ at locations G3–G6.

The smallest increase in PM_{10} concentration was found at location G4 although this was a location with a lot of traffic and traffic jams. During the measurements however, there was less traffic because adjoining streets were closed due to road works.

The higher average increase in PM_{10} concentration measured at G2 was due to some days with excessive PM_{10} concentrations compared to other days at this location. It was observed that the higher concentrations occurred at days with wind coming from north-west. The measurement system was situated at the south-east of the crossing. This intersection is one of the busiest in town. It is also possible that other sources than traffic contribute to the observed higher concentrations. It must be mentioned that at some days with excessive PM_{10} concentrations at G2, also higher background (G1) concentrations were measured (see Figure 1).

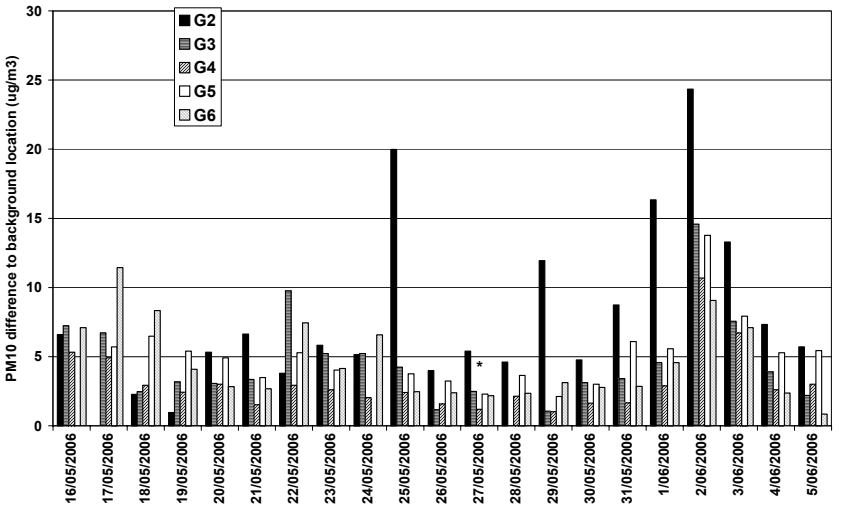

Figure 2: PM_{10} concentrations difference ($\mu g/m^3$) at five locations compared to background location G1 in Ghent. (*27/5/06: PM_{10} concentration difference compared to 44R710 because no data at background G1 was available.)

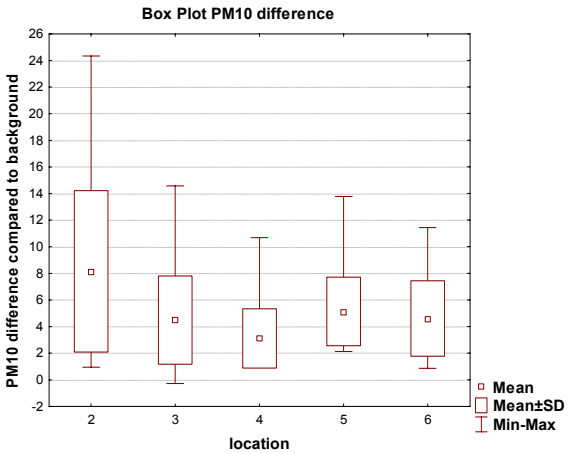

Figure 3: Distribution of the daily average PM10 difference at five locations compared to background location.

3.2 Black smoke

Figure 4 shows the black smoke concentrations ($\mu g/m^3$) measured on filter using reflection technique. Note that the resolution of this technique is not better than

1 μg/m^3. Therefore some unrealistic negative values are observed at low concentrations.

During the episode of high PM_{10} concentrations at location G2, also high concentration of black smoke are measured indicating that this is a carbon related source. The second highest values are measured at G3 and G6, representing a street canyon location and a location exposed to bus traffic.

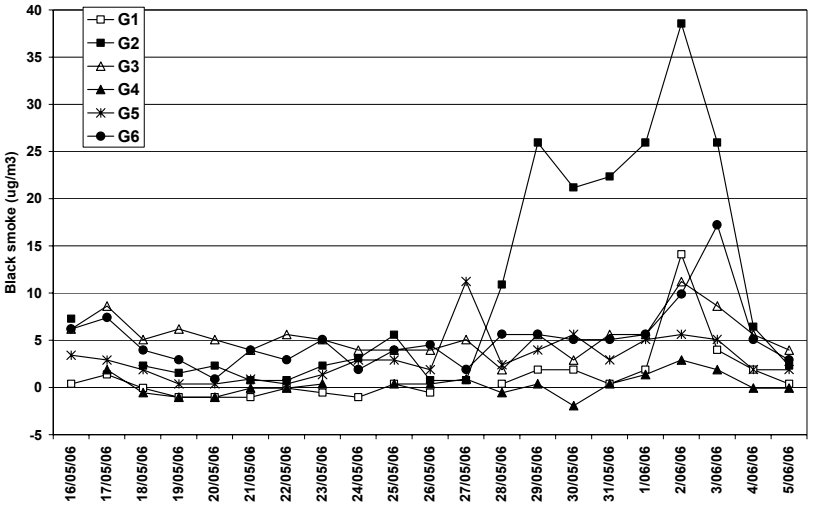

Figure 4: Black smoke concentration (μg/m3) calculated from reflection measurements on sampled filters at six locations.

Table 2: Distribution of the black smoke concentrations at 6 locations in Ghent.

Site	G1	G2	G3	G4	G5	G6
Average	1	10	5	3	0	5
Standard deviation	3	12	2	3	1	3
Minimum	-1	1	2	0	-2	1
Maximum	14	39	11	11	3	17

Black carbon concentrations measured using an aethalometer are summarised in Table 3. As already stated, measurements are not executed at the same time resulting in differences in background concentrations. Therefore, next to the black carbon concentration, also the ratio of black carbon to PM_{10} (measured with TEOM-FDMS) is given.

The highest black carbon concentration is measured at location G2. The lowest concentration is measured at the background location G1. At location G3 and G6 similar values were measured, which was also observed for black smoke concentrations.

Table 3: Black carbon concentrations measured using aethalometer at five locations in Ghent.

Site	Black carbon ($\mu g/m^3$)	black carbon / PM_{10} ratio (%)
G1	1.3	3.2
G2	3.7	8.4
G3	1.6*	6.7*
G4	2.8	5.0
G6	1.9	7.1

* results based on limited data (2 days).

3.3 NO and NO_2 concentrations

NO and NO_2 were measured at five of the six locations, during about one week each. The results are given in Figures 5 and 6. Since NO and NO_2 concentrations at the different locations are not measured simultaneously, the concentrations measured at different locations are compared to the concentrations measured at the urban station (44R701) of the air quality monitoring network.

At the background location, the concentrations for both NO and NO_2 are similar to the urban station.

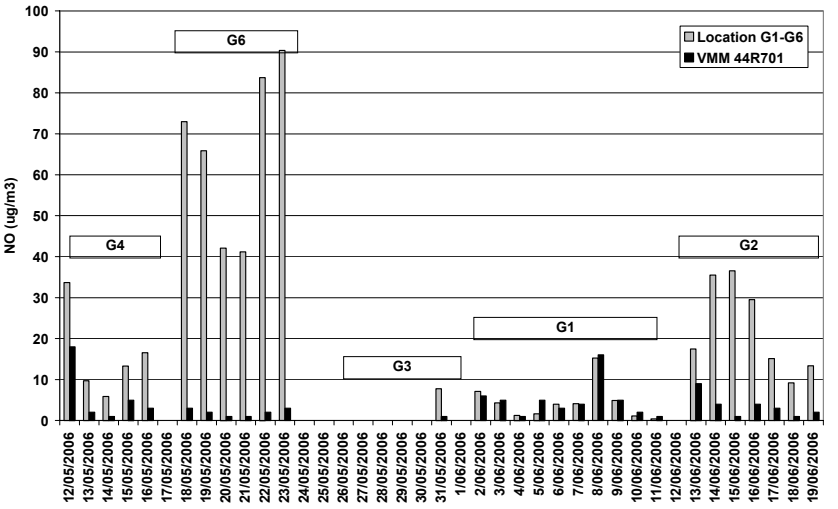

Figure 5: Daily average NO concentrations ($\mu g/m^3$) measured with monitor at five locations.

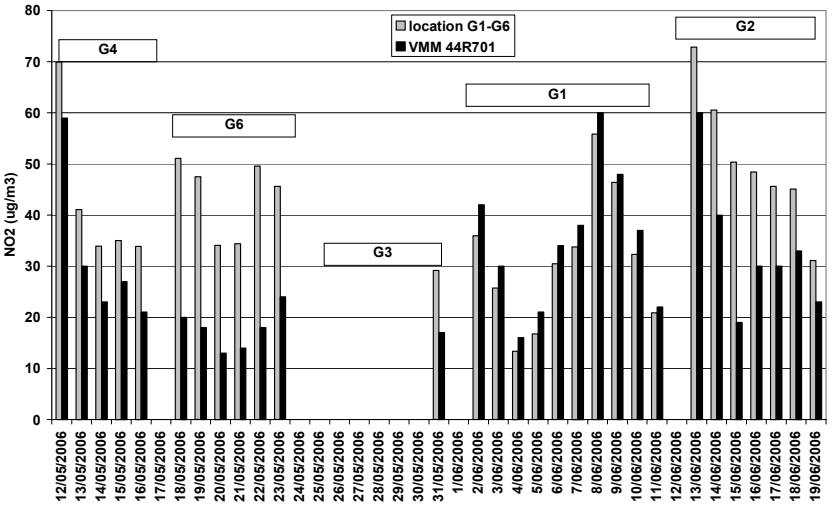

Figure 6: Daily average NO_2 concentrations ($\mu g/m^3$) measured with monitor at five locations.

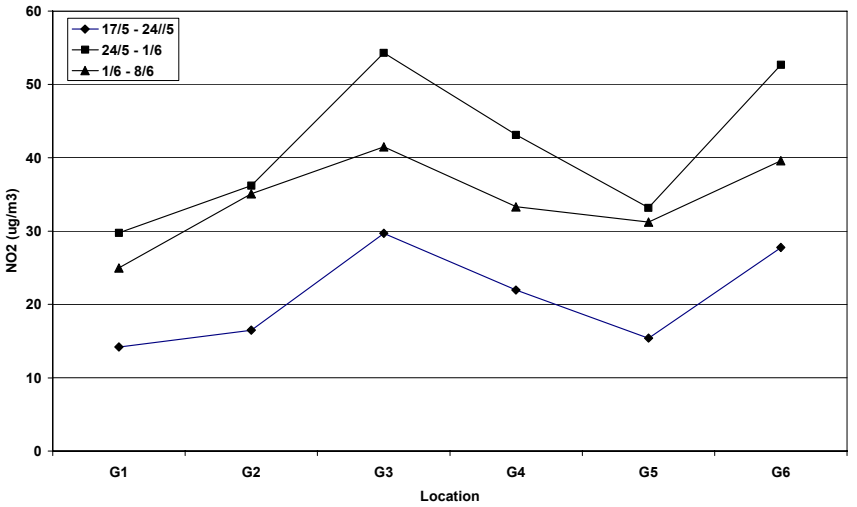

Figure 7: Weekly average NO_2 concentrations measured by diffusive samplers at six locations.

The highest excess concentration for NO and NO_2 compared to 44R701 is measured at location G6. This is possibly due to the high amount of bus traffic. The effect is more apparent for NO supporting this assumption since NOx is mainly emitted as NO. Most of the buses are not equipped with an after treatment system for NOx reduction. Insufficient data are available for location

G3. At location G2 higher concentrations are measured compared to station 44R701. At location G4, also higher concentrations for NO and NO_2 are measured.

The results of the weekly average NO_2 concentrations measured at all six locations during 3 weeks are shown in Figure 7. The same trend was found for different weeks. The lowest concentration was measured at the background location G1. Highest NO_2 concentrations are measured at G6 and G3. In the case of G6 this corresponds to the observations with the NO_x monitor (see Figure 6). For G3 insufficient data are available to compare with.

4 Conclusions

Results from a measurement campaign in the city of Ghent are presented. PM_{10} mass concentrations, NO, NO_2 and black carbon are measured.

At the background location, lowest concentrations were measured for all parameters. Differences in PM_{10} and NO_2 were observed between the different locations. It seems that NO_2 is more sensitive to traffic exposure than PM_{10}. At the bus location, highest NO and NO_2 values were measured. Highest concentrations of PM_{10} and black carbon are measured at the ring location. However some trends could not be explained.

The data presented here are part of a lager study funded by the city of Ghent. These data are used for model validation of the current situation.

Acknowledgements

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Human exposure against particles: the indoor-outdoor problem

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Abstract

Airborne particles seem to be associated with health effects. The main question is what kind of particles (ultrafine, fine — PM2.5 or PM10) cause these adverse health effects. Linked with this question is the problem of exposure pattern and/or exposure scenarios and what is the contribution to the doses coming from outdoor and indoor exposure. In urban areas, ultrafine particles primarily originate from traffic. The influence of traffic on outdoor and indoor concentrations is therefore of special interest. Within epidemiological studies the exposure situation is usually characterized using outdoor particle concentrations, despite people spending most of their time indoors. The aim of the following study was to elucidate how indoor particle size distributions correlate with outdoor concentrations in the absence of significant indoor sources. The outdoor and indoor particle size distributions were measured with scanning and differential mobility particle analyzer systems. In absence of major indoor sources total indoor particle number concentrations were always lower than outdoor concentrations. Obviously the indoor environment is generally shielded against outdoor particulates. The indoor size distributions of particles are different from outdoor ones: the concentrations of very fine particles are decreased significantly and the concentration maxima are shifted to larger diameters with respect to outdoor particle sizes. Furthermore a time lag exists in the correlation between outdoor and indoor number concentrations. Outdoor particle concentrations contribute considerably to indoor concentrations. Therefore, in the absence of actual indoor measurements, outdoor particle size distributions can be used in epidemiological investigations as a surrogate for actual indoor particle concentrations. To assess the resulting particle burden for humans, a suitably weighted average emphasizing indoor aerosol particles must be used. To classify the health effects of particles of different diameters, different reductions of particle number concentrations depending on the particle sizes must be taken into account if indoor concentrations cannot be measured and outdoor concentrations are used in place of indoor measurements.
Keywords: particles, indoor, outdoor, health relevance.

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1 Introduction

Within epidemiological studies the exposure assessment is a basic step. This paper is devoted to some remarks to a rather new research topic in environmental hygiene and exposure research, the problem of outdoor to indoor relationships for submicrometer and ultrafine particles in ambient air.

It is now generally accepted that airborne particles may cause illness but the available data does not permit the derivation of specific guidelines for particles significantly smaller than 2.5 μm in diameter. Because airborne particles do not constitute a uniform population, various measures for particulate air pollution have been investigated in epidemiological studies, the main ones being TSP (Total Suspended Particulate matter), PM10 and recently PM2.5 (Particle Mass concentration of particles smaller than 10 or 2.5 μm in diameter; Phalen [1], Schwartz et al. [2], Murphy et al. [3], Pope et al. [4], Schwartz and Naes [5]). Nevertheless, the ill-health effects of PM2.5 have also been discussed (Gamble [6], Murphy et al. [3], Pekkanen, et al. [7], Tiittanen et al. [8]).

There is a simple reason to restrict epidemiological studies to particles which are smaller than 10 micrometer in aerodynamic diameter: very large particles are not inhalable and respirable. Therefore they cause no internal burden. Particles smaller than 10 μm in diameter are on the other hand inhaled and deposited in the upper airways and the lungs. Three basic size dependent mechanisms determine efficiency and the location of particle deposition in the lungs:

Some findings suggest that particle fractions smaller than PM2.5 may be of great importance for adverse effects (Tsai et al. [9], Dreher et al. [10], Peters et al. [11], Pekkanen et al. [7], Oberdörster et al. [12]). Recently, special attention has been paid to submicron and ultrafine particles (smaller than 1 μm).

Principally, there are some simple arguments for paying special attention to particles (< 1 μm) and especially to ultrafine particles:

- Sub-micrometer and ultrafine particles may reach the deepest regions of the human respiratory system.
- Clearance mechanisms which remove inhaled particles for the lungs do not work as effectively for ultrafine particles as for larger particles.
- Compared to the mass concentrations which decreased dramatically within the last decades the number concentrations are still high or tend to increase.
- Urban traffic is a main source of these particles and urban traffic volume is increasing.
- Chemical composition of submicron and ultrafine particles may differ from larger ones because these particles originate from different sources.

Up to now most evidence for effects of these particles is based on laboratory studies (Osier and Oberdörster [13], Churg et al. [14], Murphy et al. [3], Li et al. [15], Lundborg et al. [16], Stone et al. [17], etc.). Only few epidemiological studies have paid special attention to the ill-health effects of such particles (Peters et al. [11], Pekkanen et al. [7], Wichmann et al. [18]). These studies

usually use outdoor particle concentrations and size distributions measured at one site in the city which is regarded as typical for the city. But number concentrations of particles originating from traffic differ significantly within one city (Tuch et al. [19]).

And there is an additional important fact determining the human exposure to airborne pollutants: At least in most parts of Europe people spend most of their time indoors.

Unfortunately, epidemiological studies in the field of submicron and ultrafine particles are typically restricted to measurements of outdoor particle concentrations because detailed size-resolved indoor measurements in the homes of the study population are both time consuming and expensive. Detailed knowledge of ratios and correlation between indoor and outdoor particle size distributions is therefore needed to improve the quality of exposure assessment in such studies. Here we investigated how indoor particle size distributions of submicron and ultrafine particles correspond to the outdoor concentrations in the absence of significant indoor sources.

2 Material and methods

Measurements were carried out in different buildings and rooms in different floors on the institute campus. This site is an urban background site. We also included a site which is representative for typical traffic pollution in a city centre (Voigtländer et al. [20]).

Measurements of particle size distributions have been carried out between summer 1999 and summer 2004. Two different differential/scanning mobility particle sizer systems measured particle size distributions of particles between ~15 nm and ~800 nm indoors and outdoors simultaneously (TSI 3936L10, TSI, St.Paul, MN). Outdoor particle size distributions were measured by a custom made twin differential mobility particle sizer (Birmili et al. [21]). The comparability of both systems was verified by parallel outdoor measurements.

The indoor system was installed in an unoccupied apartment on the second floor of the typical European multi family townhouse with the windows and doors closed and without active ventilation (Franck et al. [22]). To minimize the effect of indoor sources (Chao et al. [23]) during the experiments, the level of human activity was kept low. The dwelling has modern, tightly closing windows. The air change rate was estimated judging by the type of windows and the literature to be in the order of 0.2-0.4 h-1 (Reinmuth [24], Krooß et al. [25], Ihle [26], Chao and Tung [27], Koponen et al. [28]). The theoretical rate was calculated using the length of the joints of windows and door to be 0.31 h-1/0.33 h-1, respectively (DIN 4701). Additional measurements using SF6 as tracer gas yielded a mean rate of 0.16/h-1 (for method cf. Lohmeyer [29]). The same measuring conditions were used for indoor measurements at the campus site.

Outdoor measurements from a street (Tuch et. al. [30]) and from a measurement station approx. 2 km (linear distance) away (campus, IfT) were used as outdoor reference data. The outdoor system sampled from a commercially available PM10 inlet mounted 5 m above the ground at a distance

of 1 m from the wall of the building. The identical instrument at the measurement station site sampled from an identical inlet mounted on the roof of the institute building (height 13 m above the ground).

3 Results

In absence of indoor source outdoor particle number concentrations are significantly higher compared to parallel indoor measurements. A typical time series of outdoor and indoor concentrations is shown in figure 1.

Figure 2 demonstrates that particle size distributions indoors are shifted towards larger particles.

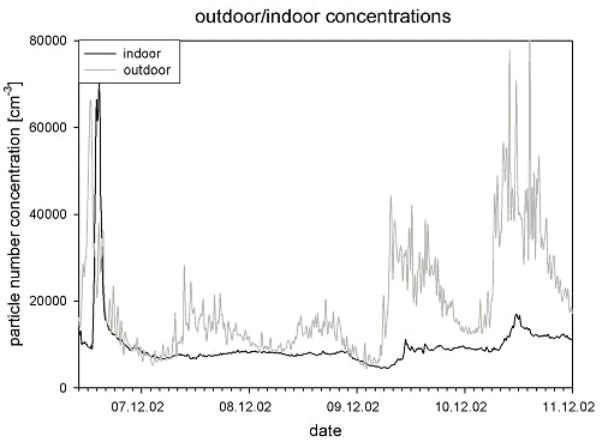

Figure 1: Indoor and outdoor total number concentrations.

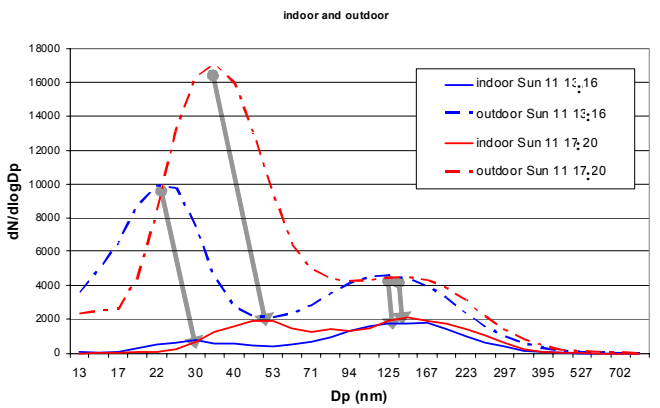

Figure 2: Simultaneously measured indoor and outdoor particle size distributions.

Indoor and outdoor concentrations are correlated. Generally, the correlation is highest between the concentrations of indoor particles of a specific size and smaller outdoor particles. We found higher correlation coefficients for a time lag between earlier outdoor measurements and indoor measurements because outdoor particles need a specific time to penetrate into the indoor environment.

Figure 3 elucidates the time dependence of the correlation between 34 nm outdoor particles and indoor particles with a diameter of 108. In this example correlation coefficient is highest for a time lag of approximately 2 h. Generally, it is the same tendency for all particle sizes: Outdoor concentrations of particles of a selected diameter exhibit the highest correlation with larger indoor particles and with a time lag which under this experimental condition was about 2 hours. It must be noted, that this time lag is more or less specific for our measurement sites. The time lag for other indoor environments depends among other things on the air exchange rate between outdoor and indoor air.

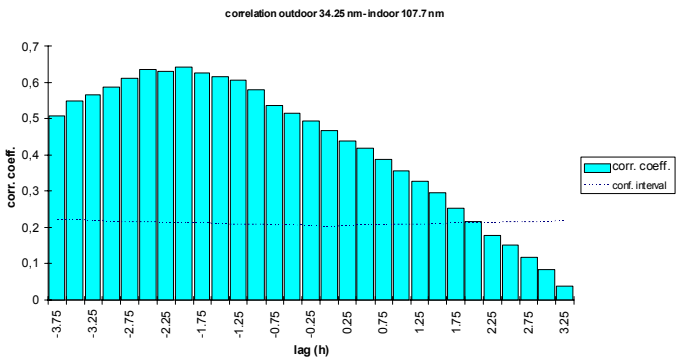

Figure 3: Correlation Coefficients of Concentrations of outdoor particles of a diameter of 34 nm with indoor particle concentrations (107.7 nm). (The lower correlation coefficients for positive times show that outdoor concentrations which are measured after the indoor concentrations do not influence the indoor concentrations or, with other words, that auto-correlation is not the basic reason for this correlation pattern.)

In studies addressing acute health effects an appropriate time lag must be added to the time lag of the health effect itself if outdoor concentrations are used as measure for the exposure of a person indoors.

Our findings demonstrate that outdoor and indoor number concentrations and particle size distribution are different. The important question for an epidemiologist is therefore:

To which share of outdoor particles humans will be really exposed indoors?

In lack of actual indoor measurements average particles size distribution shifts and typical time lags may be used to derive an average function needed to

calculate indoor exposure from outdoor measurements. Only a limited number of indoor measurements in typical homes of the study population is necessary to determine this function.

Figure 4 shows the average of about 1500 size distributions measured indoors and outdoors. The ratio between indoor and outdoor concentrations is highest for ultrafine particles.

For epidemiological studies a shielding efficiency can be calculated from such averages. This shielding efficiency is particle size dependent (Fig. 5).

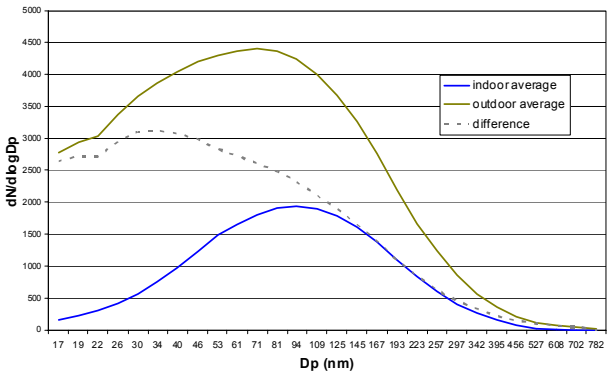

Figure 4: Averaged indoor and outdoor size distributions for sub-micrometer particles. (Data from all four seasons.)

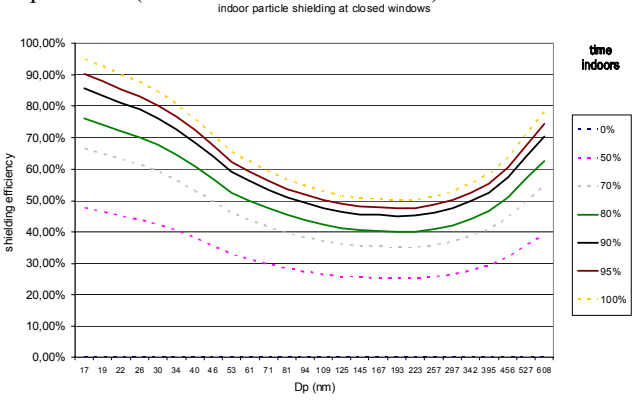

Figure 5: Exposure reduction by indoor shielding. The total shielding efficiency takes different indoor time budgets into account.

The calculated shielding efficiency can than be used to fold outdoor particle size distributions (measured earlier due to the time lag) with the appropriate curve for the time spent indoors to determine an average exposure of a population under study. If, on the other hand, only integral number or mass concentrations are of interest for a specific epidemiological study shielding efficiency curves can be integrated to calculate shielding efficiencies for such

size ranges. Using the size distribution data, two typical size fractions of aerosol can be formed: The size range from 17 nm to 109 nm represents the ultrafine fraction of PM1. For typical indoor time budgets (80 – 95 % of the day indoors) 60% to 70% of outdoor ultrafine particles do not penetrate into the indoor environment. The size range from 109 nm to 782 nm corresponds to the coarser fraction of PM1. The indoor shielding efficiency for this fraction varies between 40% and 50%.

4 Conclusion

Outdoor particles contribute to indoor particle exposure. Both indoor size distributions and concentrations are different from those measured outside. Total exposure including the time budget indoors and outdoors differs from the exposure measured outdoors.
The observed differences between indoor and outdoor exposure to particulate air pollution can be summarized by "the 3 indoor Ls":

1. LESS: The indoor environment is generally shielded against outdoor particulates, leading to lower number concentrations indoors than outdoors, if no important indoor sources are present.
2. LARGER: The indoor size distributions of particles are very different from outdoor one: The concentrations of very fine particles are decreased significantly and the concentration maxima are shifted to larger diameters with respect to outdoor particle sizes.
3. LATER: There exists a time lag in the correlation between outdoor and indoor number concentrations.

Determination of typical shielding efficiencies for the homes of a study population will help to improve exposure assessment for epidemiological studies addressing health effects caused by particulate air pollution based if real indoor measurements are not possible. If typical homes of a study population still exist this approach may even be used to reevaluate existing epidemiological studies.
The knowledge of indoor-outdoor ratios of particle concentrations is necessary for a sound description of the healthy housing quality.

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Size distribution of commuters' exposure to airborne particulate matter in buses in the UK

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Abstract

Traffic is an important source of particle emissions which contribute to urban air pollution around the world. In transport microenvironments particles of various sizes, which can be inhaled and cause serious health effects, are generated from fuel combustion. In this study, the size distribution of commuters' exposure to particles inside public buses was examined in the city of York, UK. Measurements were conducted during the winter, inside different types of buses. Particle number concentrations were measured in four main size classes: 0.3–10μm, 1.0–3.0μm, 3.0–7.5μm, and 7.5–15μm. The correlation coefficients between particle number concentrations for these different size ranges differed for each type of bus. Statistical analysis showed that the different size classes of particles were influenced by different factors. Particles in size class 0.3-1.0μm were affected by the duration at bus stops, number of people active, and outdoor concentrations, but the effect of numbers and activities of passengers in re-suspending particles was the dominant factor for coarse particles.
Keywords: transport, particles, exposure, buses.

1 Introduction

The size distribution of airborne particles is an extremely important parameter for personal exposure studies in various microenvironments. Particle size distribution is very variable both in time and space, which reflects the stability, behaviour, characteristics and chemical composition of particles.

Epidemiological evidence summarised by WHO [17] suggests that more than 280,000 premature deaths can be attributed to long-term exposure to particles in the 25 countries of the European Union (EU), while short-term exposure to particles also increases the risk of emergency hospital admissions for

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cardiovascular and respiratory diseases. There is evidence that these adverse health effects depend on particle size. Recent epidemiological studies have suggested that particles with a diameter less than 1μm (PM_1), which can penetrate into the alveolar region of the lungs, can affect lung physiology and cause a higher prevalence of respiratory disease (Issever et al. [11]; Pope [14]). Other studies suggest that reductions in the heart rate of cardiac and hypertensive patients are associated with $PM_{0.3\text{-}1.0}$, while $PM_{2.5\text{-}10}$ is significantly associated with effects in the upper parts of the airways and lungs [3].

Assessment of health effects of particles, and of the benefits of measures to reduce emissions, needs to consider the actual exposure experienced in different micro-environments. Traffic is a major source of fine particles as people travel for work, visits, shopping and other events in cities. Previous studies of personal exposure to particles in transport microenvironments have investigated both private and public transport modes, including car, bus, train, taxi, and tram (e.g. Kaur et al. [12], Gulliver and Briggs [9], Harrison et al. [10], Chan et al. [6], Adams et al. [1], Sitzmann et al. [15], Akbar and Ashmore [2]). These studies indicate that exposure to particles in transport microenvironments is higher than in other indoor microenvironments and at urban monitoring sites.

Although most of these studies have concentrated on exposure to particles in cars, bus is the most popular and frequently used public transport mode in UK cities. Previous studies carried out in the UK of personal exposure to particles in buses [1, 12] were conducted in combination with measurements in other transport modes, as was the study in Hong Kong [6]. These studies did not relate concentrations in buses to particular characteristics of the journeys. In the US, studies have focused on exposure of pupils in school buses (Fitz et al. [7]). Moreover, all these studies focused on measurements of mass concentrations, and no study has determined particle size distributions in buses. Analysis of particle size distribution and number concentration in buses could enhance understanding of how particles behave in buses and assist in assessment of the possible effects on passengers' health.

The objectives of the study were to determine the particle size distribution and number concentrations in different bus microenvironments; to compare the number concentrations of different particle size groups; and to identify significant factors which affect in-bus particle concentrations

2 Methodology

2.1 Selection of routes

Transport in York is focused on an inner ring road around the historic city centre and a number of radial roads, which link it to the outer ring road. Four typical and popular bus routes were chosen, with contrasting types of buses. On Route 1, single-decker and double-decker buses run between two suburban areas through the city centre. Route 2 is a circular route, which passes the university, hospital, and a major shopping mall, and goes through the city centre; it is operated by both single and double-decker buses. Measurements on Route 1 and 2 were

conducted in both morning and evening rush hours on weekdays, from 8:00 to 10:00 and 16:30 to 18:00. There was congested traffic, with more commuters on board than at other time periods. Route 3 services a Park & Ride facility close to the outer ring road, calling at the train station and the city centre, before returning. Two-compartment bendy buses were examined on this route. Route 4 is in a suburban environment, and connects two big shopping malls; a mini-bus is the only type of bus operated. Measurements on Route 3 and 4 were made during the peak pre-Christmas shopping period on weekends and weekdays, from 10:30 to 17:00.

2.2 Instrumentation

Continuous real-time measurements of particle number concentrations were made using a portable aerosol spectrometer (GRIMM 1.108 dust monitor [8]), which determined particle number counts in different sizes. The monitor classifies particles into 15 different size ranges. Particles are recorded with upper boundaries of 0.3μm, 0.4μm, 0.5μm, 0.65μm, 0.8μm, 1.0μm, 1.6μm, 2.0μm, 3.0μm, 4.0μm, 5.0μm, 7.5μm, 10μm, 15μm and 20μm. The monitor was held about 20cm from the breathing zone, sitting in the middle of buses. The carrying case was used to keep the monitor balanced and steady.

Travel diaries were recorded during each trip, with information that included date, time, route, bus type, bus number, seating position of monitor, number of passengers, the time trips started, number of traffic stops, number of bus stops, number of passengers getting on and off at each bus stop, particular locations the bus passed by, and window status. Data on PM_{10} concentrations at a monitoring location in the city centre, measured using a TEOM instrument, were obtained for the period of each trip [5].

2.3 Particle size classification

Data were divided into four classes based on the characteristics and behaviour of the particles and on correlation patterns in the monitoring data, using the dividing points of 1.0μm, 3.0μm, 7.5μm and 15μm. Data from the size class 15–20μm were omitted as concentrations were low and erratic.

3 Results

3.1 Overall number concentrations

Mean number concentrations of particles in the four size classes in different types of buses are shown in Figure 1. The mean number concentrations of particles in size class 0.3–1.0μm range from 73,000 l^{-1} to 141,000 l^{-1}, in size class 1.0–3.0μm range from 820 l^{-1} to 4,200 l^{-1}, in size class 3.0–7.5μm from 110 l^{-1} to 1,200 l^{-1} and in size class 7.5–15μm from 20 l^{-1} to 90 l^{-1} .

Analysis using one-way ANOVA and Tukey post-hoc tests showed no significant differences in number concentrations in the fine particle class (0.3–1.0μm) between bus types, although the highest concentrations were found

in the bendy bus and circle line bus (Figure 1). For each of the two coarse particle classes, the concentrations in the bendy bus were significantly greater than in all the other bus types. There was a tendency for higher concentrations in the single-decker buses than in the circle line and mini-buses, although this difference was not significant.

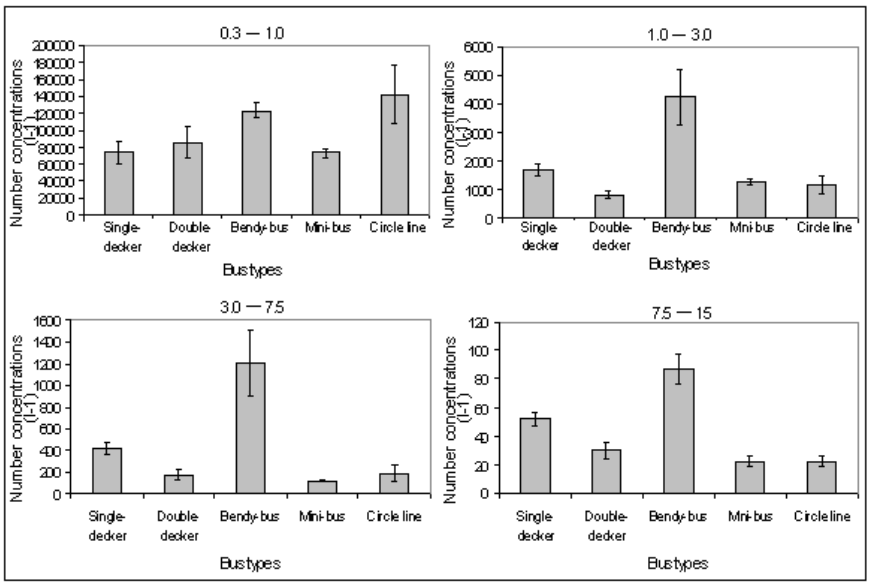

Figure 1: Mean number concentration of four particle size classes in five bus types. Error bars represent the standard error of the measurements, n = 22 for single-decker bus, n = 20 for double-decker bus, n = 24 for bendy-bus, n = 8 for circle line bus, n = 9 for mini-bus.

3.2 Correlations of four size classes

Correlation analysis was employed to assess the strength of the relationships between concentrations in different particle size classes in different types of bus. Table 1 summarizes the correlation matrices for each type of bus. All significant correlation coefficients were positive.

Concentrations in the two coarse particle classes were significantly correlated, except for the mini-bus. Concentrations in the finest particle class were never correlated with those in the two coarse particle classes, and were only correlated with those in the 1.0–3.0μm class in single-decker buses and mini-buses. The strongest difference between different types of buses is shown by concentrations in the 1.0–3.0μm class, which were strongly correlated to these of the finest class in single-decker bus and mini-bus ($p = 0.05$), and to both coarse particle classes ($p = 0.01$ or 0.05) for other types of buses. These results strongly suggest that there are different sources of particles for the different size classes.

Table 1: Correlation matrices of four particle size classes for five types of buses. Vales of n are as given in legend for Figure 1.

Single -decker	0.3-1.0	1.0-3.0	3.0-7.5
1.0-3.0	.462*		
3.0-7.5	0.314	.960**	
7.5-15	-0.161	0.368	.486*

Double -decker	0.3-1.0	1.0-3.0	3.0-7.5
1.0-3.0	0.139		
3.0-7.5	-0.104	.871**	
7.5-15	-0.068	.759**	.921**

Bendy bus	0.3-1.0	1.0-3.0	3.0-7.5
1.0-3.0	0.061		
3.0-7.5	0.081	.984**	
7.5-15	0.137	.898**	.891**

Mini-bus	0.3-1.0	1.0-3.0	3.0-7.5
1.0-3.0	.830*		
3.0-7.5	0.39	0.555	
7.5-15	-0.176	-0.281	0.567

Circle line bus	0.3-1.0	1.0-3.0	3.0-7.5
1.0-3.0	-0.345		
3.0-7.5	-0.382	.820*	
7.5-15	-0.416	.813*	.974**

* Correlation is significant at the 0.05 level (2-tailed).
** Correlation is significant at the 0.01 level (2-tailed).
*** Correlation is significant at the 0.001 level (2-tailed).

3.3 Re-suspension of particles

One possible source that might contribute relatively more to the coarser particle concentrations is re-suspension of particles by passenger activities such as walking, moving bags and touching seats when they get on or off buses. Results from Route 3, which services the Park & Ride facility, provide the strongest indication of the importance of re-suspension of particles by passengers getting on and off the bus. The example trip presented in Figure 2 was measured in the evening of 4th December 2005. The duration of the trip was about 22 minutes. There were initially 3 passengers on board when the bus departed from the Park & Ride site, 2 of them got off and 82 more got on in the city centre in the period 16:47:12 to 16:49:23.

As shown in Figure 2, number concentrations of particles in all classes increased from 16:47 and reached peaks at 16:49 or 16.50. This was the time when passengers boarded the bus in the city centre. The concentrations of coarse particles increased about 75% compared to the previous minute. This increase became progressively less marked for the finer size classes, with very little effect on concentrations in the range 0.3–1.0 μm.

3.4 Factor analysis

Multiple regression analysis was conducted to identify factors which are predictive of concentrations in different size classes, combining data for all bus types. The five factors used in this analysis are summarized in Table 2, which

also indicates the form of the data and its derivation from diary and other information. All five factors had been shown to be independent of each other in correlation analysis.

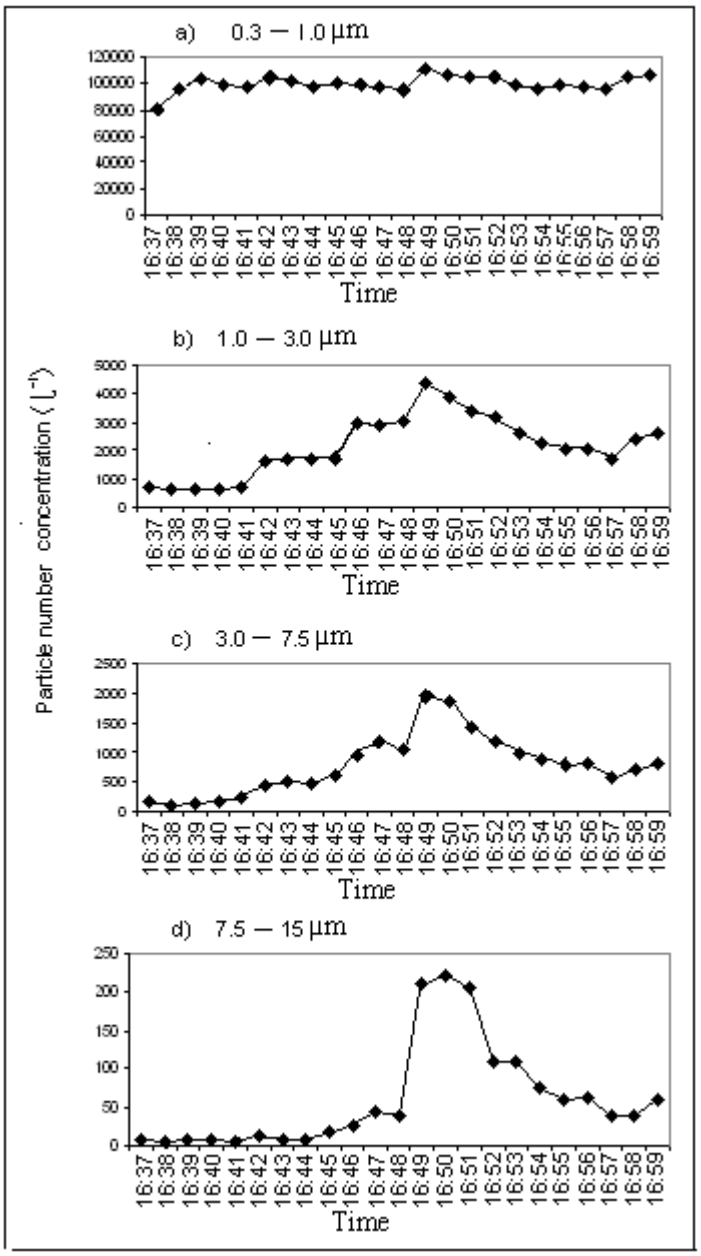

Figure 2: Time-course of particle number concentration (l^{-1}) in four size classes in the afternoon of 4th December 2005, on Route 3.

Table 2: Summary of factors, data types, and derivation of data, for multiple regression analysis.

Factors	Data type	Derive of data
Number of people active	Quantitative	Number per minute of the trip
Duration at bus stops	Quantitative	Proportion of total duration of the trip
Ambient PM concentration	Quantitative	Log_{10} transformed concentrations
Traffic stops	Quantitative	Number per minute of the trip
Time of day	Category	Code of two levels

Table 3: Summary of results of multiple regression (all bus types).

Particle size range	Model of best fit	R^2 for model of best fit
0.3-1.0	C = 4.114 + 0.687.TEOM – 1.058.DBS + 0.063NPA *** ** **	0.271
1.0-3.0	C = 2.812 + 0.071.NPA + 0.051.NBS * ***	0.290
3.0-7.5	C = 2.162 + 0.155.NPA ***	0.225
7.5-15	C = 1.355 + 0.130.NPA ***	0.321

***: P<0.001; **: p<0.01; *: p<0.05
TEOM: Log_{10} concentration at fixed site monitors (μg m^{-3})
DBS: Duration at bus stops
NPA: Ratio of number of people active
NBS: Number of bus stops

Stepwise multiple regression was performed to develop models to predict the number concentrations inside buses, using a backwards model filling procedure. All selected factors were first entered into the model, each factor was tested in turn, and the weakest factor that had the least significance was then removed. To satisfy assumptions of normality, the data of particle number concentration and ambient PM_{10} concentrations were transformed into log_{10} values.

The results are shown in Table 3. ANOVA showed that the regression explained a significant proportion of the variation in particle number concentration in each case, although only between 22% and 32% of the variation could be explained. Number concentrations in the 0.3–1.0 μm class were significantly increased by high outdoor concentrations (TEOM), and more people active on buses, while longer duration at bus stops decreased the number concentrations. The regression coefficient for outdoor concentrations was more significant than that for the other two factors. The significant factors for the 1-3 μm class were NPA and NBS, indicating that particle number concentrations were increased both by the number of passengers and by the number of bus stops. The only factor that significantly increased the concentrations of the two coarse particle classes was NPA, which is probably due to the deposition and re-suspension of these larger particles. If there were more passengers getting on or off of the bus, there would be more large particles re-suspended.

4 Discussion and conclusion

Personal exposure to particles in buses in UK cities may only cover a short exposure period compared to other microenvironments, but concentrations may be relatively high. The air exchange rate and penetration rate of outdoor air into buses may be significantly greater than for buildings, because of the frequent opening of doors at bus stops, and the use of air conditioning systems or open windows. Furthermore, the density and frequency of people's movements in a bus are much higher than in offices, day care centres and homes, and may be more comparable to school classrooms, for which high concentrations of coarse particles have also been reported (Stridh [16]). Particle concentrations in buses most likely reflect high outdoor concentrations, often in busy traffic [1], the effects of self-pollution from exhausts (Behrentza et al. [4]), and re-suspension from activities within the bus, but previous studies have not clearly distinguished the contribution of these different sources to in-bus concentrations.

The measurement of number concentrations of particles in different size classes in this study, together with recording of the characteristics of each bus trip, enabled us, for the first time, to infer the contribution of different factors to concentrations of different size particles. According to the multiple regression analysis, the activities of passengers, the number of bus stops and ambient concentrations were the main factors related to the measured concentrations in bus trips. Although only 25–35% of the variation in mean trip concentrations could be explained by the fitted regression equations, the outdoor concentrations used were only from a fixed city centre site, rather than on the particular bus routes, while passenger movements are likely to be only a crude estimate of actual levels of re-suspension. Extension of our approach to include measurements of concentrations immediately outside the bus, and detailed chemical and physical analysis of the particles, would allow more definitive assessment of the contribution of different sources.

Many previous measurements of personal exposure to particle mass concentrations provide mean values over durations of 8 to 24 hours (e.g. Mohammadyan and Ashmore [13], Stridh [16]), but assessment of the health significance of in-bus exposures must rely on measurements over the period of the actual trip. The study of Adams et al. [1] in London used a high flow personal sampler to measure fine particle ($PM_{2.5}$) concentrations in bus trips of about 1 hour duration. The mean personal exposure of 39 $\mu g\ m^{-3}$ was similar in summer and winter and bus concentrations were consistently higher than in car and bicycle trips on the same route. Exposures were significantly higher on trips in the centre of the city, where outdoor concentrations would be higher. However, personal exposures for trips on the same route using buses with open and closed backs were similar, suggesting, as in our study, that penetration of outdoor air was not the only factor affecting in-bus concentrations. A further study in a specific location in central London [12] reported a similar mean personal exposure to $PM_{2.5}$ in buses (34.5 $\mu g\ m^{-3}$), and that this was three times higher than concentrations at a local urban background monitoring station and

50% higher than at a local kerbside monitoring station. High ultra-fine particle counts were also found on buses

Although the exposure durations for these studies in buses in London were only about an hour, the $PM_{2.5}$ exposures exceeded 24h mean guidelines for protection of human health set by WHO [17]. Much higher concentrations have been reported on bus trips in Delhi [2]. The results of our study in York suggest that the significance for human health of in-bus exposures will depend on the sources of the particles of different sizes to which passengers are exposed. Since vulnerable groups, such as the elderly and children, tend to be over-represented in bus journeys in the UK, and since government policy seeks to increase use of public transport models such as buses, there is a need to carefully assess the factors influencing exposure to particles in bus trips and their significance for public health.

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A comparison between aerosols modelled and measured by AERONET network emitted by vegetation fires over Iberian Peninsula

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Abstract

This work aims at validating the CATT-BRAMS model which can simulate emissions and transport of aerosol and trace gases from forest fires which occurred in the Iberian Peninsula on the period from 7 to 12 August 2003. The validation of the generated aerosol concentrations values was made by comparison with AERONET (Aerosol Robotic Network) aerosol optical thickness (AOT) measurements at two different wavelengths, which is a quantity that is related to the aerosol load in the atmospheric column.
Keywords: aerosol optical thickness, Angström exponent, transport model, biomass burning.

1 Introduction

Forest fires in Europe are a major source of concern for environmental security. Every year several hundred thousand hectares are burned throughout European forests. These fires put at risk, not only human life and property but also the sustainability of forests and other woodlands. The regeneration of vegetation after fire, mainly in the Mediterranean area, can be slow and consequently

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favours the erosion and soil loss processes. Hence, it is important to do a yearly assessment of the total surface burned and of the type of land cover affected to estimate the damage.

Summer 2003 was one of the most severe fire seasons experienced during the last decades in Southern Europe. Record temperatures across Europe, reaching over 40 C in some countries, caused some of the worst forest fires ever seen stoked forest fires from Poland to the Iberian Peninsula. According to the European Forest Fires Information System (Schmuck et al. [1]) the total area of forest burnt was 647,069 hectares - four times the size of Greater London. More than half (390,146 hectares) were in Portugal, making it the worst forest fire season the country had faced in the last 23 years. Spain registered during the same period extreme temperatures of 46°C in the south and 51°C in the city of Sevilla. Forest fires burning 70 kilometers east of Madrid and in Salamanca destroyed about 2.000 hectares of forest.

This work aims at validating the CATT-BRAMS model which can generated aerosol concentrations values produced by forest fires occurred in the Iberian Peninsula during the period 7-12 August 2003. The validation of the generated aerosol concentrations values was made by comparison with AERONET (Aerosol Robotic Network) aerosol optical thickness (AOT) measurements at two different wavelengths (440 nm and 870 nm), which is a quantity that is related to the aerosol load in the atmospheric column.

2 Data and methods

2.1 AERONET data

NASA's AERONET (AErosol RObotic NETwork) program consists of a group of ground-based remote sensing instruments in the United States that can determine the amount of aerosols, or tiny particles of pollutants, that are in the air over a given location. The goal of this ground network is to assess the optical properties of aerosols, specifically how much sunlight they scatter and absorb, and to provide a double-check of aerosol data as gathered by satellites. The network imposes standardization of instruments, calibration, and processing. Data from this collaboration provides globally distributed observations of spectral aerosol optical depths, inversion products, and precipitable water in geographically diverse aerosol regimes. Episodes of forest fires aerosols are identified by increases in aerosol optical thickness particularly in 440 nm and 870 nm wavelengths and decreases in the Angström turbidity parameter (Angström exponent) – indicating larger aerosols. Descriptions may be found of program objectives, affiliations, the instrumentation, operational issues, data products, database browser "demonstrat", research activities, links to similar data sets, NASA EOS links and personnel involved in AERONET.

For the area under study, the available data is located at two sites, one at Évora city (38.5678ºN; 7.9115ºW), Portugal and the other one at El Arenosillo city (37.105ºN; 6.73347ºW), Spain. The site Évora is located in the south-western part of the Iberian Peninsula, in a rural area, remote from sources of

industrial pollution, 100 km away from the Atlantic coast. The station El Arenosillo is located in Huelva province in the south-west Atlantic coast of Spain (see figure 1). El Arenosillo is surrounded by a pine tree forest and is located within Donana National Park, a protected coastal area.

Figure 1: The location of the AERONET network over Iberian Peninsula: Évora city, in Portugal and El Aeronosillo city, in Spain.

2.2 Description CATT-BRAMS Model

The on-line 3-D transport model follows the Eulerian approach being coupled to the Brazilian developments on the Regional Atmospheric Modeling System (BRAMS) 3.2 version (http://www.cptec.inpe.br/brams). The RAMS is a multipurpose, numerical prediction model designed to simulate atmospheric circulations spanning in scale from hemispheric scales down to large eddy simulations (LES) of the planetary boundary layer. The equation set used is the quasi-Boussinesq nonhydrostatic equations described by Tripoli and Cotton [2]. The model is equipped with a multiple grid nesting scheme which allows the model equations to be solved simultaneously on any number of interacting computational meshes of differing spatial resolution. It has a complex set of packages to simulate processes such as: radiative transfer, surface-air water, heat and momentum exchanges, turbulent planetary boundary layer transport and cloud microphysics. The initial conditions can be defined from various observational data sets that can be combined and processed with a mesoscale isentropic data analysis package (Tremback et al. [3]). For the boundary conditions, the 4DDA schemes allow the atmospheric fields to be nudged towards the large-scale data. New deep and shallow convective schemes based on the mass flux approach and with several types of closure (Grell and Devenyi [4]) were also implemented.

The biomass burning source emission parameterization (for CO, CO2, CH4, NO_x and $PM_{2.5}$) is based on the MODIS fire observation and field observations. For each fire detected by remote sensing, the mass of emitted tracer is calculated and its emission in the model follows a diurnal cycle of the burning (Freitas et al. [5]). The type of vegetation that is burning is obtained from the IGBP 1km vegetation map, thus allowing an appropriate selection of the vegetation dependent factors in mass emission estimation.

The sources are spatially and temporally distributed and daily assimilated according to the biomass burning spots defined by the satellite observations. The carbon monoxide emission associated to the anthropogenic processes (industrial, power generation, transportation, etc) is provided by EDGAR database (http://arch.rivm.nl/env/int/coredata/edgar/). All biomass burning emissions are added with the EDGAR "agricultural waste burn" and "fuelwood burning" emissions with 1x1 degree horizontal resolution and 1 year time resolution. For $PM_{2.5}$, the tracer convective transport scheme accounts also for the wet (in and below cloud) deposition based on the work of Berge [6].

2.2.1 Model configuration, initial and boundary conditions

The initial and lateral boundary conditions necessary to drive CATT-BRAMS were provided by the twice daily Aviation run of the National Centers for Environmental Prediction Global Spectral Model (AVN) with a resolution 1.25 x 1.25 degrees. The model is set up with two tri-dimensional grids. The coarse grid specification was defined with 80 km grid spacing and the other two with 20 km, both centered at 38.8°N; 9.28°W (Lisbon). The vertical resolution starts at 150 m near the surface, stretching at a rate of 1.10 to a final resolution of 850 m, with the model top at about 21 km. The time step was 60 s for grid 1 and 30 s for grid 2.

The BRAMS full microphysics package was activated for all the grids. This scheme includes the use of generalised gamma distributions as the basic function for all hydrometeor species; the use of a heat budget equation for hydrometeor classes, allowing heat storage and mixed phase hydrometeors (Walko et al. [7]). Grell cumulus parameterization scheme improved by Grell and Devenyi [4], radiation parameterization from Chen and Cotton [8], turbulence and diffusion parameterizations were handled using the Mellor and Yamada [9] was activated in two grids. Topography, vegetation type, land percentage and sea surface temperature were read onto the grid from USGS (U.S. Geological Survey at 1km horizontal resolution) datasets. The simulation utilized silhouette-averaged topography (Bossert [10]) in order to incorporate the desired terrain effects. A soil model was assumed, using seven levels with 50% saturation moisture for all depths (Tremback and Kessler [11]) and constant inflow conditions are used to the tracer boundary condition and the emission sources of biomass burning aerosols were obtained from the MODIS/TERRA fire product combined with local observations made available for Europe.

3 Results

During the first half of August 2003 a severe heat wave hit Western and Central Europe. The persistent anticyclonic conditions characterized by exceptionally high temperatures low values of relative humidity with average flow presented a predominant direction northwest over Iberian Peninsula were favourable to the development of a large-scale pollution episode. The stagnation of the air mass also led to the accumulation of the primary emitted particulate matter (PM) and the development of secondary aerosols (Vautard et al [12]). Furthermore, in conjunction with the dry, hot weather conditions, the Southern part of Europe was influenced by significant forest fires that generated a huge amount of primary particles, principally in Portugal (EFFIS).

Figures 2 and 3 show the times series of aerosol optical thickness from AERONET in the 440 nm and 870 nm wavelengths, Angström exponent and modelled column concentration of $PM_{2.5}$ ($\mu g.m^{-2}$) simulated by CATT-BRAMS in Évora city, Portugal and El Arenosillo city, Spain, respectively, on the period from 7 to 12 August 2003. The results show a good agreement between modelled aerosol concentrations and the aerosol optical thickness at 440 nm and 870 nm measured at Évora, although the agreement is better at the smaller wavelength. This can be explained since at smaller wavelengths the aerosol optical thickness is larger and more sensitive to smaller particles, which is normally the case of burning-originated aerosols.

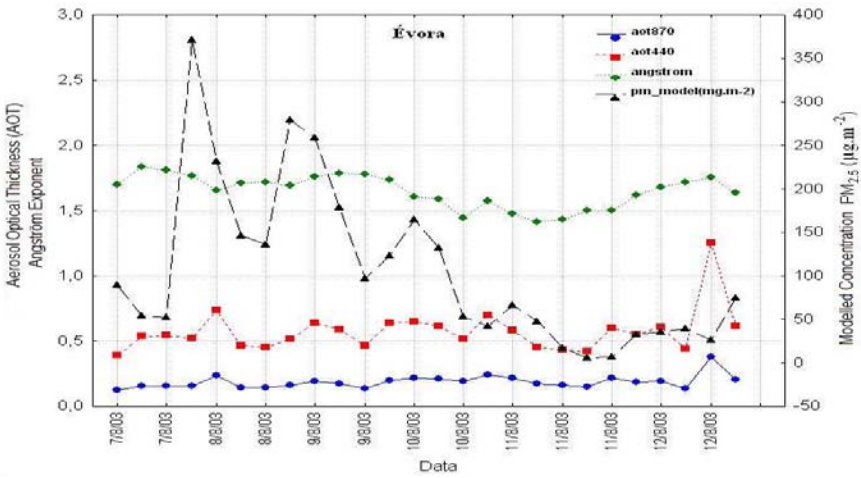

Figure 2: Time series of aerosol optical thickness from AERONET in the 440 nm and 870 nm wavelengths, Angström exponent and modelled column concentration of $PM_{2.5}$ ($\mu g.m^{-2}$) simulated by CATT-BRAMS in Évora city (38.5678ºN; 7.9115ºW), Portugal on the period from 7 to 12 August 2003.

For El Arenosillo the situation is quite different since a mixture of different aerosol types are present: together with biomass burning aerosols, generated at the south of France and Spain an intrusion of desert dust aerosols appears on the 8 August followed by a decrease on the 11 August. The modelled aerosol concentration is relatively low; due to the fact the fire sources were located far away from El Arenosillo with distinct meteorological conditions, whereas at Évora site the fire sources were located close to the site.

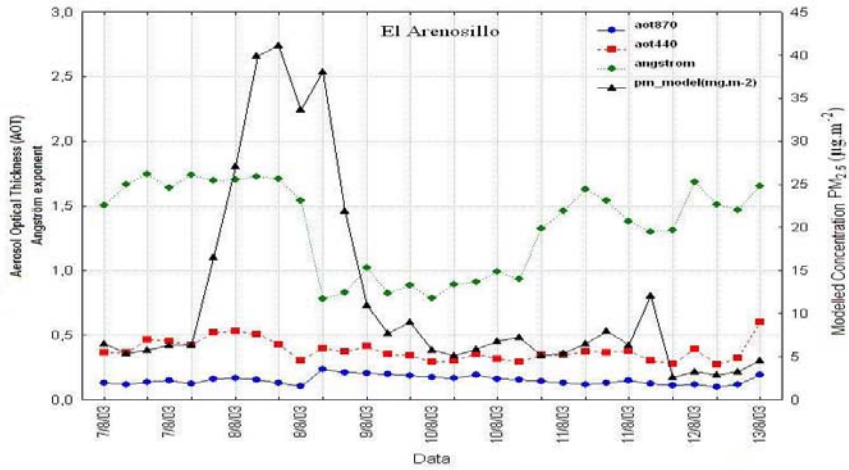

Figure 3: Time series of aerosol optical thickness from AERONET in the 440 nm and 870 nm wavelengths, Angström exponent and modelled column concentration of $PM_{2.5}$ ($\mu g.m^{-2}$) simulated by CATT-BRAMS in El Arenosillo city (37.105ºN; 6.73347ºW), Spain on the period from 7 to 12 August 2003.

4 Conclusions

The general performance of the model presented in this paper, lead to believe that the mesoscale models are a useful tool to simulate aerosol concentration values, reasonably well, in comparison with the aerosol optical thickness at two wavelengths measured at the same sites where modeled values were generated. The sources emission from biomass burning and technological activities for several gases and aerosol may be defined from several published dataset and remote sensing. The biomass combustion emits gases and aerosol particles that interact efficiently with the solar radiation affecting the microphysical processes, dynamics of cloud formation and air quality. The contamination caused by fires can reach distant areas from the burned region and -o increase the pollution from the urban and industrial sources. Therefore, the understanding and fires impact evaluation through numeric modelling is possible and may identify the interrelations between biosphere and atmosphere characterizing a multi-disciplinary study.

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Generation of monodisperse aerosols through condensation nuclei control

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Abstract

A device for the generation of monodisperse aerosols through condensation nuclei control has been designed and tested in the present study. A continuous flow, evaporation-condensation aerosol generator has been designed to produce monodisperse aerosols of low vapor pressure organic liquids, such as dioctyl phthalate (DOP), at flow rates over 2.5 lpm. Nebulised NaCl particles are passed through the particle number controller to reduce the number concentration close to 10^5/cc to suppress homogeneous condensation. The condensation nuclei with nitrogen as a carrier gas are passed through a bubbler containing DOP, producing a nuclei–vapor mixture. The mixture is condensed producing the aerosols of narrow size distribution. A heater section previous to the condenser section provides complete evaporation across the tube diameter, while the condenser walls in free convection create a low temperature gradient, both of which enhance aerosol monodispersity. The results show that controlling the nuclei number concentration as well as vapor source can produce aerosols with sufficient monodispersity.

Keywords: condensation nuclei, evaporation, condensation, monodisperse aerosol.

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1 Introduction

An important element of aerosol technology is the production of test aerosols for calibrating instruments, conducting aerosol research, developing and testing air cleaning and air sampling equipment. Monodisperse aerosols are used to calibrate particle size measuring instruments and to determine the effect of particle size on sampling devices. A monodisperse aerosol is usually defined as an aerosol that has a geometric deviation of less than 1.2. In aerosol research, monodisperse test aerosols of known size, shape and density are highly desirable because most aerosol properties depend strongly on particle size, which is best controlled by using monodisperse aerosols. Tests made with a series of monodisperse aerosols, each having a different particle size, permit the evaluation of the effect of particle size on aerosol properties or the performance of an instrument. Test aerosols also used for various types of inhalation studies, such as studies of animal exposure to toxic substances, respiratory deposition in humans or animals and the administration of therapeutic aerosols [3].

Understanding the fundamental mechanisms of aerosol nucleation and growth has long been a central problem in aerosol science. Such understanding has important implications in characterizing and controlling fine particle emissions from combustion systems and in elucidating the dynamic processes governing the formation and growth of atmospheric aerosols. In simulating atmospheric aerosol dynamics, for example, it is desired to predict the rate of new particle formation as a function of the rate of generation of condensable vapor by gas-phase chemical reactions. Predicting rates of new particle formation in the atmosphere requires consideration of the effect of both preexisting particles and newly formed growing particles on the vapor and cluster concentrations in the system Simultaneous homogeneous nucleation [5].

Sinclair and La Mer [8] first described the generation of aerosols by controlled condensation of vapour upon nuclei. Di-2-ethylhexyl sebacate (DEHS), an organic liquid with a low vapour pressure at room temperature acts as aerosol substance. Since DEHS is insoluble in water and known as non-toxic, its aerosols can be inhaled by a human being and used for deposition studies of particulate matter in the human respiratory tract

Aerosols with particle sizes below 10 μm may be generated by condensation. A stream of nuclei is exposed to the vapour of a low-volatile liquid at an elevated temperature, and the controlled heterogeneous condensation of the vapour onto the nuclei results in the formation of the product aerosol [2].

For particle sizes down to 0.1 μm the use of aerosol generators of the La Mer-Sinclair type provides monodisperse aerosols. Other types of condensation aerosol generators were used by many authors to generate aerosols with particle sizes below 0.1 μm But most of this system--heated wire generator exploded wire generator high intensity arc generator plasma torch generate polydisperse or low concentrated quasimonodisperse aerosols with decreasing concentrations with time.

The use of electrically heated tube furnaces to vapourize the aerosol material show the possibility of the generation of highly concentrated aerosols by means

of homogeneous condensation. The particle sizes range down to 1 nm with long time stability but with size distributions with geometric standard deviations of $\sigma_g \lesssim 2.5$ i.e. polydisperse aerosols.

Monodisperse aerosols are obtained after electrostatic classification. The high concentrations and the relative small size distributions of the primary condensation aerosols provide classified monodisperse aerosols with concentrations between 10^3 and 10^6 particles/cm ^{3} for particle diameters down to 2 nm [7].

For some applications, such as instrument calibration, a monodisperse aerosol is desired. There is however no precise definition of a monodisperse aerosol, i.e. how small a spread of particle sizes constitutes "monodisperse". As most generated aerosols have a lognormal distribution, the geometric standard deviation, σ_g, can be used as a measure of the monodispersity. That is, an aerosol, which has σ_g less than about 1.22, could be assumed monodisperse. This arbitrary definition has no rigorous justification, but can be used as a rough indicator. Most so-called monodisperse aerosol generators can produce aerosols with $\sigma_g < 1.1$ [6].

Milos et al, [4] have described a generator for producing monodisperse aerosols. The process involves atomizing the aerosol material (dioctyl phthalate was used) to form a polydisperse aerosol, which is rendered uniform by vaporization and condensation. The principle is similar to that used by Rapport and Weinstock and by Preining [4], but it has been found that by extracting a small percentage of the aerosol from the center of the stream from the condensing tube, a more monodisperse aerosol could be obtained. It is also found that dissolving the DOP in alcohol and could easily vary the size of the DOP aerosol by varying the solution concentration. Thus, with DOP concentration ranging from 0.001 to 100 per cent the size of the DOP aerosol could be varied from 0.036 μm to 1.3 μm dia.

The device developed for the generation of monodisperse aerosols can be used for the study of air pollution effects at the laboratory level, as the effect of aerosol is size dependent.

2 Experimental setup

The experimental setup used for the production of monodisperse aerosol by evaporation—the condensation process is shown in figure 1. Using the nebuliser, a very dilute NaCl solution is sprayed from a nozzle to produce droplets. Upstream of the nebuliser, a diffusion dryer removes the water from the droplets to produce small crystals, depending on the original concentration of the solution. The particle number controller permits lowering of the concentration of the salt crystals from the original value, before the crystals are used as condensation nuclei in a heterogeneous condensation process. Since the concentration of the final aerosol is approximately same as concentration of the nuclei aerosol, the particle number controller can be used to control the aerosol concentration within the boundaries imposed by the heterogeneous condensation

process. The size of the aerosol particles is determined by the quantity of available vapor per nucleus. The number concentration of the nuclei is set by the flows in the particle number controller.

The saturation of the gas, with vapor from the aerosol material, takes place in the bubbler. The nuclei aerosol bubble through the aerosol material at a constant temperature. Depending on temperature and vapor pressure, a certain saturation concentration of the vapor is achieved in the bubbler. The bypass around the saturator allows dilution of the saturated gas. This permits rapid adjustment of particle size by changing the ratio of bypass to total flow rate, rather than by waiting to heat or cool the saturator.

The nuclei–vapor mixture is re-heated, in the reheater section, to ensure that no condensation takes place upstream of the condensation chimney. In the condensation section, the vapor–nuclei mixture is cooled down in a laminar flow and the resulting supersaturation causes the vapor to condense onto the nuclei.

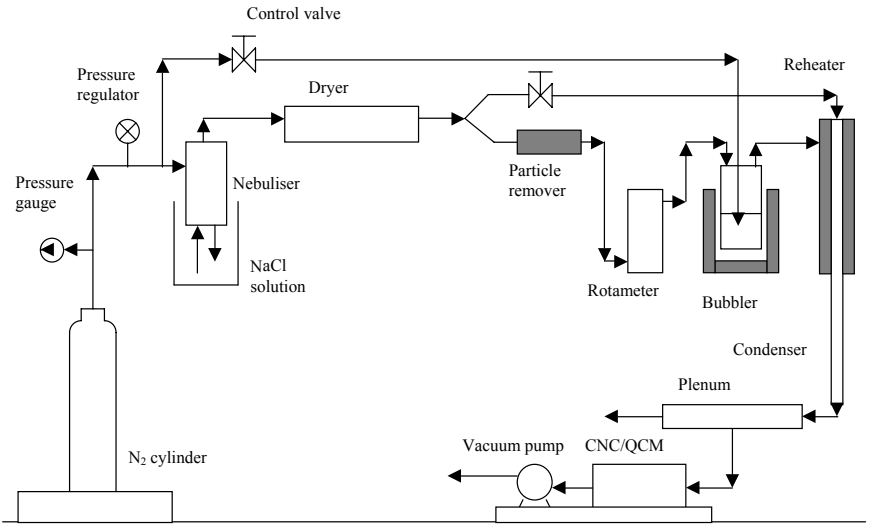

Figure 1: Experimental setup to generate monodisperse aerosols.

2.1 Aerosol measurement technique

Size segregated particulate mass was measured by cascade impactor with Quartz Crystal Microbalance (PC-2 QCM, California Measurements, INC, USA). The sampling flow rate is 1.5 lpm. The impactor has ten stages and segregates aerosol samples into ten size ranges between 25 and 0.05 μm. The manufacturer reported the cut sizes for the impactor for spherical particle of density 2 gcm^{-3}. However, these cut diameters are different from the values reported in the calibration studies on the instrument [1]. In this study, the cut sizes of the impactor were adopted from Horton et al. [2]. The performances of the crystals were stable and satisfactory for the aerosols generated by aerosol generator. The aerosol concentrations observed on stages having cut sizes greater than 3.1 μm were very

low and found to be statistically unreliable. Therefore, only the mass measured by stages having cut sizes less than 3.1 μm are used in our assessment.

3 Results and discussion

The control over the number concentration of condensation nuclei close to 10^5/cc is achieved with the help of particle remover. It is clear from the table 1 that, the diffusion battery is having very less collection efficiency compared to the particle remover which is having a collection efficiency of 71.42% (12 mg/l and 24 mg/l) with steel wool of diameter 0.15 mm and 91.42% (12 mg/l and 24 mg/l) with plastic fiber of diameter 0.14 mm. Since the particle remover with plastic fiber is having higher collection efficiency compared to the diffusion battery and the steel wool, particle remover with plastic fiber is used throughout the experiment

The size distribution of the initial NaCl nuclei measured after passing through dryer is shown in figure 2. The initial NaCl nuclei have a MMD of 0.26 μm and probably number distribution peaks. This is ideal for generating particles in the sub micron range. The low vapor pressure liquid, DOP is then vaporized and condensed over the NaCl nuclei in the condenser section of the experimental setup. The size of the NaCl is increased due to the condensation process and is shown in the figure 3. The monodispersity is achieved by controlling the flow condition in the condenser tube.

Table 1: Condensation nuclei number concentration.

NaCl Concentration: 12 mg/litre

Pressure (kg/cm^2)	Flow rate (lpm)	Value position	Number concentration per cc		
			Diffusion battery	Particle remover	
			1000 tubes (1mm diameter)	Steel wool (0.15 mm diameter)	Plastic fiber (0.14 mm diameter)
1.8	1.5	Closed Opened	5×10^5 7×10^5	2×10^5 7×10^5	6×10^4 7×10^5

NaCl Concentration: 24 mg/litre

Pressure (kg/cm^2)	Flow rate (lpm)	Value position	Number concentration per cc	
			Particle remover	
			Steel wool (0.15 mm diameter)	Plastic fiber (0.14 mm diameter)
1.8	1.5	Closed Opened	2×10^5 7×10^5	6×10^4 7×10^5

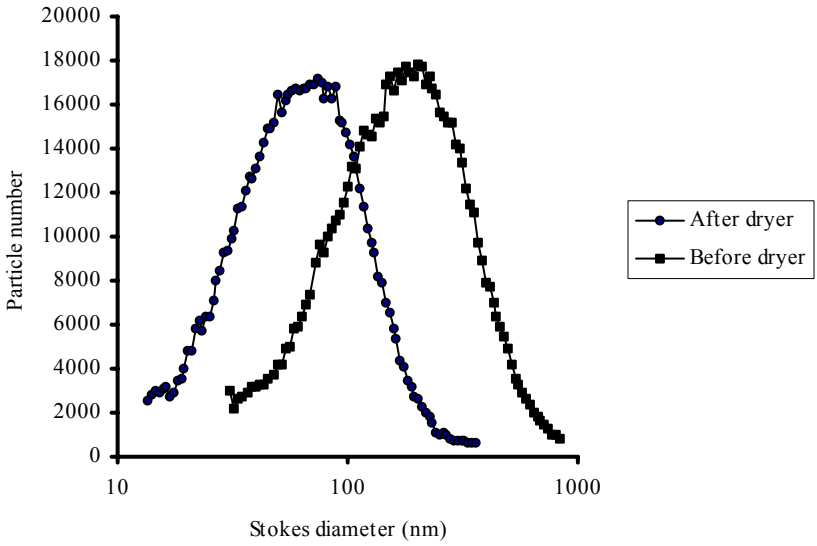

Figure 2: Particle size before and after dryer.

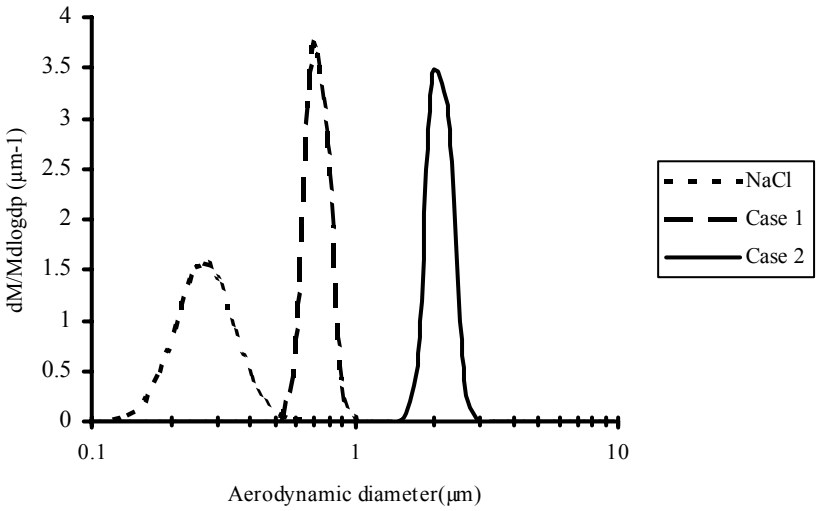

Figure 3: Mass size distributions of initial NaCl nuclei and aerosols after condensation of DOP vapour.

For case 2 the temperature of the bubbler is 200 ˚C and flow rate through the bubbler is 1.5 lpm, whereas for case 1 the temperature of the bubbler is 150 ˚C and the bubbler flow is 1.5 lpm with the operating pressure 1.8 kg/cm^2. The

increased bubbler temperature generated more vapor available for condensation with same number of nuclei, hence caused the increase in diameter compared to case 1. The both cases showed good monodispersity but the study is limited by the size resolution of the instrument used in the experiment. The results obtained are comparable with the results of Horton et al. [2].

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Assessment of particle pollution in an industrial area in Kuwait

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Abstract

Particles less than 10 μm in diameter, which are named as respirable particle (RPM) by the OSHA have very low sedimentation speeds under gravity, and may remain in the air for days before eventually being washed out by rain or impacted out onto vegetation or buildings. RPM are a very important environmental pollutant, which can causes visibility, surface soiling, and health problems. Therefore, it is necessary to find concentrations of the RPM in ambient and working places. This paper will discuss a study of PM10, PM2.5 and RPM in an industrial area of Kuwait. This area houses several construction material industries such as cement bricks, marble products, paving products etc. Due to the industrial nature, an intensive amount of dust is generated in the confined working environment. The sampling sites included indoor and outdoor areas. Sampling periods were from cold to hot weathers. Thus, comparisons under different weathers, different locations, and in-out doors can be made.
Keywords: air pollution, PM10, PM2.5, respirable particle, health effect.

1 Introduction

There are many particles floating around in the air, some of which cannot even be seen. Particles can be solid particles or liquid droplets. They are ranged from 0.1 to 50 μm which are called total suspended particles (TSP). The small particles less or equal to 10 μm can be further divided into two major groups according to sizes: coarse particles (PM10) and fine particles (PM2.5). Particles less than 10 μm in diameter tend to pose the greatest health concern because they

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can be inhaled into and accumulate in the respiratory system. Therefore, it is necessary to find the size distribution and concentration of the particles (less than 10 μm) in air.

Maximum limit allowance for occupational exposure to particulates set up by Kuwait EPA is 5 mg/m^3 for respirable dusts, which are less than 10 μm (RPM) [1]. The standard for nuisance dusts from US Occupational Safety & Health Administration (OSHA) [2] is also 5 mg/m^3. The conditions for the OSHA standard are limited as the particles containing no asbestos and quartz less than 1% and penetrating non-ciliated portions of respiratory system.

The Clean Air Act (CAA) in US was passed in 1970, and the National Ambient Air Quality Standard (NAAQS) was established. In the NAAQS, TSP was one of the 7 criteria pollutants. The USEPA standard for particle matter changed from TSP to PM10 in 1987. PM2.5 was subsequently added to the new standard in addition to PM10 in 1997. PM2.5 is a subset of PM10. The PM10 is classified as inhalable fine particulate matter by USEPA [3].

The USEPA air quality index (AQI) for particle matter includes both PM10 and PM 2.5 (see Figure 1) [3]. It should be noticed that the definition for inhalable particle is different between USEPA and Kuwait EPA. The Kuwait EPA definition for inhalable particles is particles whose diameters are large than 10 μm.

US EPA continuously renews the NAAQS standard. Particles less than 2.5 μm have gained more and more attention. The unhealthy levels (AQI > 151) can provide more information for assessing the health problems caused by dusts in air.

An industrial area is located northwest of Kuwait city. It houses several small construction material industries such as cement bricks, marble and granite cutting and polishing and paving products. Due to the nature of this type of industry, intensive amount of dust is generated in the confined working environment (Figure 2). Most, if not all, of the work are conducted manually. Therefore, labours may be exposed continuously to high level of dust in the work surroundings. According to an internationally accepted respiratory tract model [4], inhaled particles larger than 10 μm (micron) will be cleared from the lungs by mucociliary action, swallowed, and eventually reach the gastrointestinal tract, whereas, particles less than 10 μm can be deposited in the respiratory systems. The accumulation of such particulates due to continuous and long time exposure can lead to an increase of the level of pollutants and radioactive materials in the respiratory system and other body organs, accordingly leading to severe adverse health effects. Although heavy metals are not attracted to single biological compound, previous research has demonstrated that they have toxic effects on specific organs in the body. For this reason limits were implemented on toxic elements and compounds by Law No. 21 of 1995 in Kuwait [1], and a special attention has also been paid to the composition of building materials [5,6].

The US EPA AQI related to PM10 and PM2.5 concentrations are listed in Table 1.

Several ambient air pollution studies have been conducted by Kuwait EPA, Kuwait Institute for Scientific Research, Kuwait University, and other private

companies; however air pollution in the working environment need more investigations. Since Kuwait Environmental Protection Agency (EPA) has issued the environmental regulation in October 2001 (Maximum Limits Allowance Table for Biological Effect – as a result of occupational exposure to chemical substances), it is essential to investigate the particles related environmental problems in more details, in Kuwait.

Table 1: AQI and PM concentration.

AQI	PM2.5 μg/m^3	PM10 μg/m^3
0-50	0.0-15.4	0-54
51-100	15.5-40.4	55-154
101-150	40.5-65.4	155-254
151-200	65.5-150.4	255-354
201-300	150.5-250.4	355-424
301-500	250.5-350.4	425-504
>500	350.5-500.4	505-604

Index Values	Levels of Health Concern	Cautionary Statements
0-50	Good	None
51-100*	Moderate	Unusually sensitive people should consider reducing prolonged or heavy exertion.
101-150	Unhealthy for Sensitive Groups	People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion.
151-200	Unhealthy	People with heart or lung disease, older adults, and children should avoid prolonged or heavy exertion. Everyone else should reduce prolonged or heavy exertion.
201-300	Very Unhealthy	People with heart or lung disease, older adults, and children should avoid all physical activity outdoors. Everyone else should avoid prolonged or heavy exertion.
301-500	Hazardous	People with heart or lung disease, older adults, and children should remain indoors and keep activity levels low. Everyone else should avoid all physical activity outdoors.

Figure 1: US EPA AQI for particulates and health caution.

Figure 2: A workshop of a marble company in the AIA.

This paper includes PM10, PM2.5 and RPM collected and analyzed in 15 stations in the industrial area. The results have been compared to OSHA, Kuwait EPA and US EPA standards. Health effects to human beings by particle matters have been assessed.

2 Experiments

2.1 Field sampling locations

The design of this study includes comparison of PM10 and PM2.5 particles in concentrations between indoor and outdoor at the same location, outdoor and outdoor at different locations, indoor and indoor at different locations, and working and no working periods at different locations. 15 stations have been selected, which included marble company, block company, asphalt company etc. A location close to a mosque was selected as an ambient station for reference purpose.

2.2 Field sampling

Dichotomous samplers (Model 241, Andersen Instruments, Inc. Atlanta, GA USA) were used in this study. These instruments meet all the USEPA federal reference method performance specifications for the measurement of PM10 and PM2.5 [7]. Figure 3 shows a Dichotomous sampler in a block workshop.

Here, we have to emphasize that there are many semi-volatile compounds in the atmosphere which exist in particle phase [8]. These particles are easily lost during sampling. The Dichotomous sampler cannot collect those semi-volatile compounds. Therefore, the quantifications of the total particles (PM10 and PM2.5) have errors. At this moment, we cannot determine the size of the error.

Figure 3: A Dichotomous sampler in a block workshop.

2.3 Laboratory studies

The collected Teflon filters were return to laboratory for quantitative measurements of particle phase by a new Toledo balance (detection limit 0.1 μg). The metal contents and radionuclide elements were measured by an ICP and a gamma-spectrometer.

3 Results and discussions

3.1 Mosque location (Station 1)

As discussed above, the location close to a mosque was used as an ambient station to evaluate the particulate air pollution in the industrial area; and as a reference station to find the possible relation to the working places. The sampling period was from January to June 2005. In Kuwait, January and February are normal cold and relative hot in May and June. The study period generally covered the Kuwait climatic partner.

Figure 4 is a comparison of PM2.5, PM10, and the Kuwait RPM Standard. The "Quality" column is used to compare the measured RPM results and the Kuwait EPA standard for industrial area, which is 350 μg/m^3. It can be seen that more than 70% of the measured RPM were exceeding the Kuwait ambient standard for industrial areas. According to Kuwait EPA regulation, exceedance of daily average can only occur once per year. Therefore there is no doubt that the particle pollution in this industrial area is a very serious problem. At this moment, Kuwait does not have a PM2.5 standard. US EPA's standard is 40 μg/m^3 for 24 hours. If using USEPA standard as a tool, it can be seen that the exceedance of PM2.5 is also very high in this industrial area.

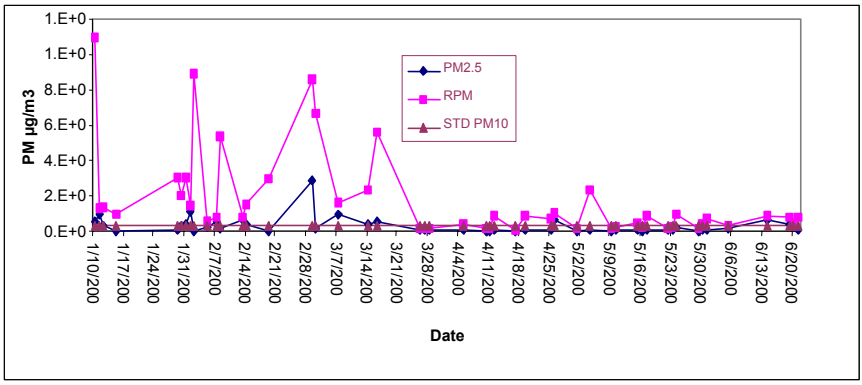

Figure 4: Comparisons of RPM and PM2.5 collected in the Station 1 with Kuwait PM10 standard.

3.2 Particulate matter in a block manufacture company (Station 2)

The product of this company is blocks. Sand and cement are the major materials used for the manufacture. We installed two samplers inside and outside the workshop. The workshop is semi-closed, which means there is an open-door in front of the workshop. There will be air exchange between outdoor and indoor airs, but not substantially. There are traffics in the front yard and a mixing machine for the sand and cement with water.

The outdoor sampler was used to monitor the ambient air in the front yard of the manufacturer to compare the air quality inside the workshop and the mosque location.

Table 2 lists the 24-hour measurement results for the indoor and outdoor. It is observed that the indoor concentrations of RPM were sometime higher and sometime lower than the outdoor, which indicates that the dusts concentrations are depended on human activities. For example, more traffic in the front yard might generate more dusts. Thus the average RPM concentrations outside the workshop sometimes were higher than inside. However, the overall average RPM concentrations inside were higher than outside due to the confined situation inside.

As discussed above, the measurement periods were 24 hours in the above study. If using USEPA AQI standard to evaluate the health effects in the above studies, it can be clear seen that except March 26th and April 5th measurement outdoor, all other RPM concentrations were in the “Hazardous” range, which requests that everyone should avoid all physical activity in this air polluted condition.

We also conducted working and non-working hours study in this location. The study results will be discussed in another section.

The comparison of RPM concentrations measured in the Station 1 and 2 is shown in Figure 5. Generally speaking, there is no doubt that the ambient particle pollution will affect the outside concentration in Station 2. When the

ambient RPM concentrations were high, the RPM concentrations outside the workshop were high. However, the outside RPM concentrations were also governed by the human being activities in the front yard. That is why sometime the outside RPM concentrations in Station 2 were higher than in Station 1.

Table 2: Particulate matter in the Al-Ayoub Company of Constitutive Materials.

Date	Outdoor μg/m^3		Indoor μg/m^3	
	PM2.5	RPM	PM2.5	RPM
12-Jan	114	2955	176	2231
15-Jan	164	7614	23	5925
31-Jan	249	1115	314	2950
2-Mar	159	1033	494	3760
7-Mar	1843	2391	1035	2511
16-Mar	660	3148	586	2477
26-Mar	6	32	42	1311
5-Apr	94	174	149	7601
Average	411	2307	352	3596

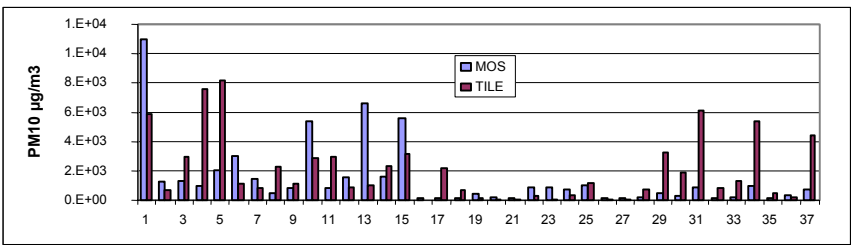

Figure 5: RPM concentration comparison between Station 1 (Mosque) and outside Station 2 (block company).

3.3 Particle matter in working and non-working hours

Particle matter in working and non-working hours were measured in most stations. Table 3 lists the measurement results. According to Kuwait EPA standard for working place, it can be observed that several manufacturers had exceeded the standard. But if using USEPA AQI as a tool to assess the particulate pollutants, it can be observed that most working places had significant health problems.

The RPM comparisons for working and non-working hours are shown in Figure 6. Generally, the RPM and PM2.5 concentrations during working hours were higher than the non-working hours. But, in several locations, it was via verse. It is noticed that these locations had large open place between indoor and outdoor, wind could easily blow dusts between indoor and outdoor, which might be the reason for the higher dust concentrations in non-working hours.

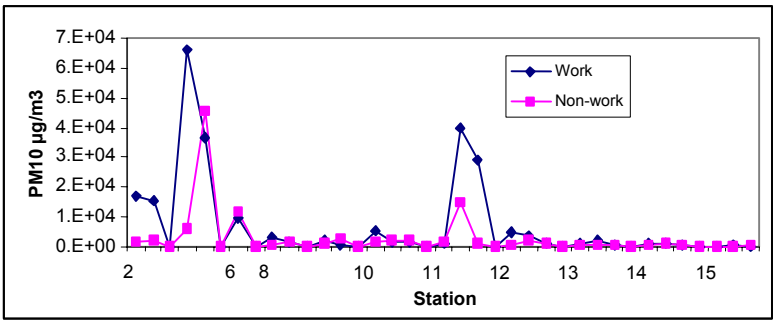

Figure 6: Comparison of RPM during working hours and non-working hours.

Table 3: Working place particle matter in Kuwait.

Station	Working Hours µg/m^3		Kuwait EPA	Non-working Hours µg/m^3		RPM 24 Hour	AQI
	PM2.5	RPM	WTA	PM2.5	RPM	Average	Category
2	486	16736	Exceed	38	1418	5901	Hazardous
	837	15437	Exceed	299	2079	12098	Hazardous
5	24000	66190	Exceed	322	5602	23141	Hazardous
	816	36816	Exceed	123	45758	43236	Hazardous
6	102	9384	Exceed	290	11599	10468	Hazardous
8	150	3221		39	789	1619	Hazardous
	43	1754		69	1552	1623	Hazardous
9	32	1915		25	1063	1354	Hazardous
	15	734		92	2822	2091	Hazardous
10	89	5081	Exceed	60	1414	2954	Hazardous
	29	1574		49	1924	1817	Hazardous
	32	1573		48	2056	1912	Hazardous
11	44	1038		88	1772	1478	Hazardous
	490	39778	Exceed	80	14913	22825	Hazardous
	470	29333	Exceed	437	1095	10080	Hazardous
12	143	4747		30	688	2183	Hazardous
	85	3468		118	2202	2681	Hazardous
	37	1321		49	1272	1286	Hazardous
13	32	1257		14	493	827	Hazardous
	44	2306		152	481	1279	Hazardous
	86	424		17	463	446	Hazardous
14	50	850		25	733	778	Hazardous
	40	1223		26	837	985	Hazardous
	19	707		25	731	722	Hazardous
15	120	202		126	129	147	
	410	443		76	156	218	
	20	20		398	423	335	Un-health

As it is well known that PM10 particles can stay in the air for minutes or hours while PM2.5 particles can stay in the air for days or weeks that is why we can find in many cases that the PM2.5 concentrations have no substantial difference between working hours and non-working hours.

3.4 Metal contents and radionuclide elements in the particles

The following metals were identified and measured in the industrial area: Cr, Fe, Ni, Pb, and Zn. It is observed that several locations had a few higher concentrations for Fe, Zn, Ni and Pd. Basically; metals are not substantial problems in the industrial area.

Many natural radionuclide elements have been identified in the samples, which include Be-8, Pa-234m, Pb-214, Th-234, K-40, Ra-226, Bi-211 etc. Fortunately the radiation was very low. Based on many standards, it is safe to say that the natural radiation in the industrial area has no significant health impact to human health.

4 Conclusions

Ambient RPM concentration is a serious problem in the industrial area of Kuwait. It requires a comprehensive plan to improve the ambient air quality in this area. Respirable dusts in the working place were different from manufacturer to manufacturer. According to Kuwait EPA standard for the working places, it was found that several locations had exceedances in the study period. But if using USEPA AQI standard as an assessment tool, the problems of dusts in the working places need to be carefully considered. A review meeting for the particulate matter in air is needed in order to clear confusions in definition and to determine the proper limitations in Kuwait.

Acknowledgements

We would like to show our deep appreciation to Kuwait EPA for participating and supporting this study. Our thanks also give to staffs from CAL for technical assistance and Mr. S. AlZoabi, Mr. M. Shlash, and Mr. Al-Saleh from CAD of Kuwait Institute for Scientific Research for field job.

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Identification of particulate matter and vitreous fibres in the atmosphere of a megacity

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Abstract

This paper reports the preliminary results of our investigation. The levels of organic carbon, elemental carbon and PTS with their relative relationships and evidence of presence of man-made vitreous fibres are reported and discussed. These preliminary results underline the importance and the necessity of a systematic approach in such studies.
Keywords: particulate matter, man-made vitreous fibres, elemental carbon, urban pollution.

1 Introduction

The characterization of atmospheric particulate matter and man-made vitreous fibres represents a very important aspect for the air quality evaluation and for their relative effects on the population both in industrial areas and in a megacity.

The particulate, also called "aerosol" or "dust", is constituted by all the suspended non-gaseous material present in atmosphere. From the dimensional point of view the definition of the various kind of particulate contemplates four categories, according to the dimension of the particle aerodynamic diameter (d_a): ultrafine ($d_a \leq 0.1$ μm); fine (0.1 μm $\leq d_a \leq$ 2.5 μm); coarse (2.5 μm $\leq d_a \leq$ 10 μm); total particulate matter (>10 μm). The particulate matter with aerodynamic diameter up to 50 μm is commonly called as particulate suspended matter (PTS). The chemical particle composition (carbonaceous fraction, organic fraction, metals, etc.) results important for the sanitary-toxicological aspect. In particular carbonaceous aerosols have been the focus of the attention in recent years because of their properties and their ubiquitous presence in atmosphere. Usually, carbonaceous aerosol constituents are classified into elemental carbon (EC), or

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black carbon, and organic carbon (OC), fractions differing for their chemical-physical properties [1,2]. The OC represent the amount of the carbonaceous particulate matter that can be oxidised at 350°C (oxidation of HC to CO_2) and has both primary and secondary origin.

Primary particulate OC is formed during combustion and associated mainly as submicron particles. In fact, mechanical processes involved in the emission of plant spores and pollen and vegetation debris, produce coarse primary organic aerosol particles [3]. Particulate OC has also a secondary origin from gas-to-particle conversion of volatile organic compounds in atmosphere, either as effect of the condensation of low vapour pressure volatile organics or resulting from physical or chemical adsorption of gaseous on aerosol particle surfaces [4,5].

EC has a primary origin, in fact it is basically an anthropogenic pollutant emitted as a result of incomplete combustion of fossil and carbonaceous fuels. EC constitutes the fraction of carbonaceous aerosols that can be oxidized at a temperature of 750°C. The sum of OC and EC represents the total carbon (TC), i.e. the total carbonaceous fraction present in the atmospheric particulate.

A fibre is defined as a particle with an aspect ratio, i.e. a ratio of the length to the width of a particle, greater than 3:1. Fibres which are 5 μm or longer and have a diameter of less than 3.0 μm are considered breathable, due to their dimensions they are capable of being inhaled and deposited deep into the lungs. The International Agency for Research on Cancer (IARC) classified in 1987 asbestos as carcinogenic for humans, group 1 [6].

Owing to its thermal and mechanical properties, together with its wear resistance, asbestos had been widely used in several merceological sectors, till it was banned by the law n. 257 in 1992 [7]. After this year, in industrial and civil applications the man-made vitreous fibres (MMVFs) have been used.

From a toxicological point of view, in 1998 IARC classified the asbestos' substitutes as possibly carcinogenic to humans (group 2B) because their potential human carcinogenic effects whereas in 2002 it confirmed the ceramic fibres in the group 2B and the other fibres (e.g., glass wool fibre) were not classifiable as to theirs carcinogenicity to humans (group 3) showing no human carcinogenic effects.

In this contest, considering the sanitary importance to be exposed to the particulate matter and airborne fibres, a study focused to the simultaneous determination of these two pollutants in the urban area of Rome. In this paper are reported the results of an intensive measurement campaign performed in a frame of a project focused to the investigation of the particulate matter composition in megacity.

2 Experimental

2.1 Sampling sites

Aerosol and fibres samples were collected in the Pilot Station located at the ISPESL's building in downtown Rome, near S.M. Maggiore Cathedral, (Figure 1): the area is characterized by anthropogenic sources

Figure 1: Sampling site in downtown Rome.

2.2 Measurement method

The separation of EC and OC was carried out by means an Ambient Carbon Particulate Monitor 5400 (Rupprecht & Patashnik Co Inc., Albany, NY, USA) based on a two step combustion procedure. During the first step, i.e. pre-combustion step, the samples were heated up to the first operating temperature (350°C). When the first desorption was completed, the sample was further burned at 750°C in order to perform EC measurement. By means a non-dispersive infrared detector (NDIR) the instrument measures CO_2 amounts released both two steps.

The total mass particulate matter was monitored by a TEOM Ambient Particulate Monitor (R&P). Both the two instruments were equipped with a PM10 sampling head.

2.3 Fibres analysis by Scanning Electron Microscopy

The fibre sampling and analysis are performed according the ISO/FDIS 14966 International Standard regulation where both the characteristics and the chemical composition of the asbestos and synthetic inorganic fibres are described [8]. The sampling for the fibre analysis was performed in two different periods: for 13 days in November 2002 and for few days in December 2002. For each day 16 samples of 90-minutes long are collected. All the sampling was performed by a sequential sampler (CF 20) using metal filter and polycarbonate filtering membrane with 25 mm diameter and 0.8 μm porosity.

All of the samples were analyzed by a Scanning Electron Microscopy (SEM) (LEO 440 S) couplet with an X-ray Energy Dispersion Spectrometer (EDS) (INCA Energy 400).

These samples were divided in two groups, one related to the diurnal period (from 7.00 to 20.30) and one to the night period (from 20.30 to 7.00) for evaluating the differences between the activities performed during the studied periods.

3 Results and discussion

In researches involving the characterization the choice of the sampling site is very important: the place is strongly influenced by anthropogenic emission sources (autovehicular traffic, domestic heating, etc.) and, no in direct way, by natural emission fluxes (biogenic sources). Further, the ISPESL building is located in a narrow street delimited by tall blocks and the wind circulation is typical of a tunnel situation.

In Table 1 are reported the concentration levels of OC, EC and PM10 ($\mu g/m^3$) determined at the ISPESL Pilot Station during the campaign. As shown, EC ranges between 5.2 and 14.9 $\mu g/m^3$ whereas OC between 4.8 and 10.2 $\mu g/m^3$. From a qualitative point of view the EC/OC ratio is always above 1 except November 9th and 11th: this i san index of an higher contribution of the anthropogenic emission on the carbonaceous fraction instead of those due to the physical–chemical transformations producing secondary organic carbon.

Table 1: Levels ($\mu g/m^3$) and ratios (%) in Rome.

	OC	EC	TC	PM10	EC/OC	EC/PM	TC/PM
09/11/03	5.7	5.2	10.9	22.5	0.91	23.0	48.4
10/11/03	6.9	6.9	13.8	39.1	1.00	17.6	35.3
11/11/03	6.3	6.1	12.4	35.4	0.97	17.1	34.9
12/11/03	10.2	14.9	25.1	54.1	1.46	27.6	46.4
13/11/03	6.3	6.4	12.7	45.8	1.02	14.0	27.8
14/11/03	7.2	8.0	15.2	85.4	1.11	9.3	17.8
15/11/03	6.9	7.8	14.7	49.4	1.13	15.8	29.8
16/11/03	7.0	8.8	15.7	40.6	1.26	21.6	38.7
17/11/03	6.3	7.2	13.5	65.5	1.14	11.0	20.5
18/11/03	7.0	8.2	15.2	59.2	1.17	13.9	25.7
19/11/03	6.4	6.5	12.9	50.4	1.02	12.9	25.6
16/12/03	6.0	7.4	13.4	45.1	1.23	16.4	29.7
17/12/03	4.8	5.4	10.2	30.9	1.13	17.5	33.0

In Table 1 the last column reporting the ratio between total carbon and PM10 is very interesting: in fact, in downtown Rome TC represents a fraction ranging from 18% to 48% of the PM10. Furthermore, from the same table the EC/PM10 ratio can be still derived (9÷27%): this shows that the contribution to the anthropogenic fraction in urban areas is averagely 20% of the total particulate matter composition. Combining these two latter considerations we can affirm that an autovehicular traffic reduction affects only the EC carbonaceous fraction whereas it does not influence the total mass because a lot of different species contribute to it.

In Figure 2 the PM10, OC and EC trends are reported from December 14th to 17th. As it can be seen there is good agreement among the curves: in particular, the correlation factor (R) between OC and EC is 0.883 and the two species have

their behaviours almost overlapping. Further, the temporal trends of EC and PM10 are very similar (R is 0.901) even if the PM10 levels are obviously higher than the EC values for presence of other species such as sulphate, nitrate, metals, etc. Basically, the daily PM10 and TC variations are related to the emission fluxes from the autovehicular traffic but are strictly connected with radon level modulation considered as tracer of the dynamic of the boundary layer evolution [9]. Finally, during the diurnal hours of the 16th it should be noted that a PM10 peak (120 μg/m^3) was observed as well the highest fibre concentration.

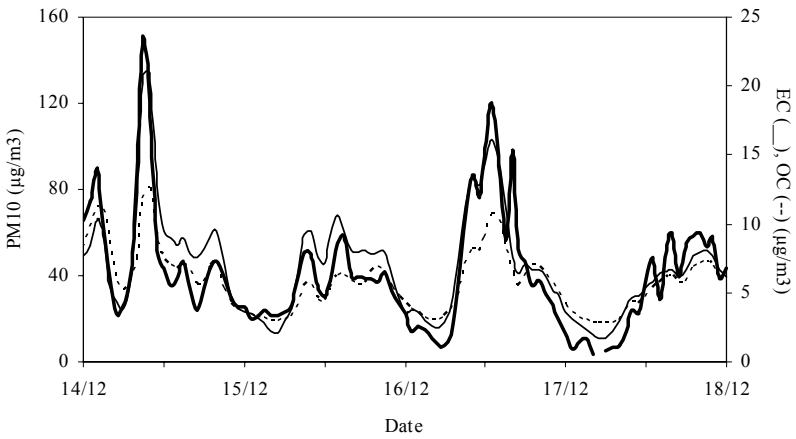

Figure 2: PM, EC and OC in downtown Rome.

Table 2: MMVFs concentration and number in Rome.

Date	Concentration (F/l)		Vitreous fibre (n)	
	day	night	day	night
09/11	0.12	0.053	0	0
10/11	0.25	0.10	0	0
11/11	0.08	1	0	1
12/11	0.16	0,1	2	0
13/11	0.08	0.1	0	0
14/11	0.12	0.053	0	0
15/11	0.12	0.10	1	0
16/11	0.041	0	0	0
17/11	0.12	0	1	0
18/11	0.2	0.1	0	0
19/11	0.12	0.053	0	0
16/12	0.12	0.053	0	0
17/12	0	0	0	0

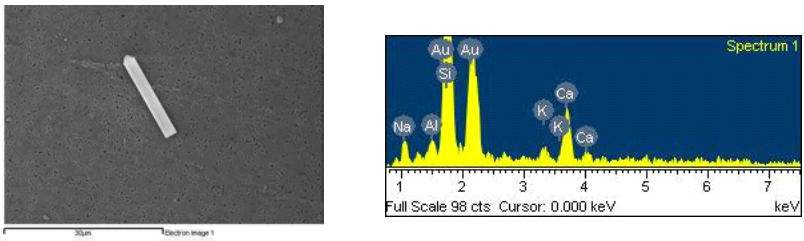

Figure 3: Glass wool fibre.

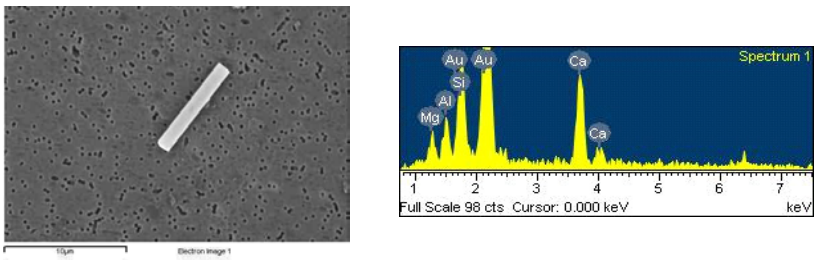

Figure 4: Rock wool fibre.

In Table 2 are reported the fibre concentrations (F/l) and the vitreous fibre number during the same day and night periods considered above. The first consideration is no asbestos fibres to be present in any analyzed samples. During the fall campaign some MMVFs are evidenced with different composition, e.g. glass wool fibres (Figure 3) and rock wool fibre (Figure 4). Furthermore, some inorganic fibres are found with chemical composition quite similar to the MMVFs (calcium silicate, iron and chromium) but with dissimilar morphology: in any case, the Ca_2SO_4 fibre number is very low and consequently there is no influence on the results.

It should be underlined that in the analyzed fibres a high fibre concentration is found in some periods: we can assume a stability atmospheric condition favouring the pollutant persistence in air.

The results obtained are related only at a single seasonal campaign performed during a fall period which is characterized by frequent raining influencing the particulate matter level and the dust sedimentation. For these reasons other campaigns will be conducted during a dry and hot period and simultaneously in areas not directly influenced by anthropogenic sources such as in side a green park.

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Section 7
Climate change and air pollution

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Global climate change – the technology challenge

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Abstract

Anthropogenic emissions of greenhouse gases, such as carbon dioxide, have led to increasing atmospheric concentrations which are at least partly responsible for the roughly 0.7°C global warming earth has experienced since the industrial revolution. With industrial activity and population expected to increase for the rest of the century, large increases in greenhouse gas emissions are projected, with additional and potentially substantial subsequent global warming predicted. The paper provides a brief overview of the factors driving CO_2 emissions for the world and for selected countries, an examination of key technologies that would be required for an aggressive mitigation program, and a concise sector-by-sector summary of mitigation options, along with R&D priorities.

1 Introduction

The Intergovernmental Panel on Climate Change [1] concluded in 2001 that anthropogenic emissions of greenhouse gases, such as carbon dioxide (CO_2), have led to increasing atmospheric concentrations which are to be at least partly responsible for the roughly 0.6°C global warming earth has experienced since the industrial revolution. Since 2001, warming has now increased to an estimated 0.7°C (NCAR [2])

In Figure 1, IPCC [1] has summarized historical and projected trends for atmospheric concentrations of CO_2. In order to make these projections, the Panel evaluated a range of scenarios, including alternative business-as-usual cases and various mitigation scenarios. As Figure 1 shows, the projected concentrations can be as high as 1000 ppm compared to a pre-industrial level of 280 ppm and a

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current level of 382 ppm. This increase in CO_2 concentration and the contributions of other greenhouse gases are the major driving force for global warming.

The author will now discuss the factors that lead to increasing emissions of CO_2 and the anticipated contribution of key countries. Then, CO_2 emissions will be projected into the future for key sectors. Finally, the author will summarize the state of the art of key technologies and R&D priorities for each of four key sectors that can contribute to mitigating such emissions. (Not that in this paper, all CO_2 concentrations will be in ppmv and all warming will be realized or transient warming, as opposed to equilibrium warming.)

Although, the scope of this paper is limited to a consideration of technologies that could play a major role in reducing CO_2 emissions, it is important to note that availability of key technologies will be necessary but not sufficient to constrain emissions. Since many of these technologies have higher costs and/or greater operational uncertainties than currently available carbon intensive technologies, robust policies will need to be in place to encourage their utilization.

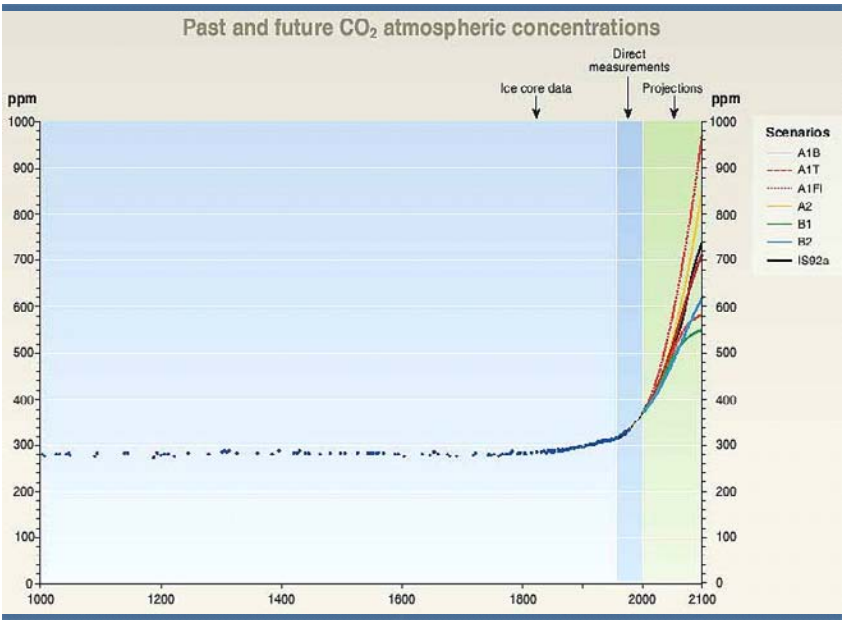

Figure 1: Past and projected atmospheric concentrations of CO_2.

2 Factors that drive emissions of CO_2

The World Resources Institute [3] has examined the factors that have driven CO_2 emissions for key countries in the 1992 to 2002 time period. The factors

considered are: Gross Domestic Product (GDP) *((Purchasing Power Parity (Intl $))*, growth per capita, population growth, carbon intensity growth per unit of energy (more coal in the mix increases this factor), and the growth of energy usage per unit of GDP. The sum of these factors approximates the annual CO_2 emission growth rate. The author has used the Institute's data to generate Figure 2, which shows how these factors have influenced the annual growth rate of CO_2 for selected countries during this ten-year period. As can be seen for the *world*, despite *decreases* in the energy use per unit of GDP, the CO_2 growth rate was about 1.5% per year. The rate for the *U.S.* also has been about 1.5%, but the growth rate for *China and India* has been about 4% per year, driven by economic growth, and for India, population growth as well. Note that in the absence of significant decreases in energy use per unit of economic output, CO_2 emission growth rates would have been substantially greater.

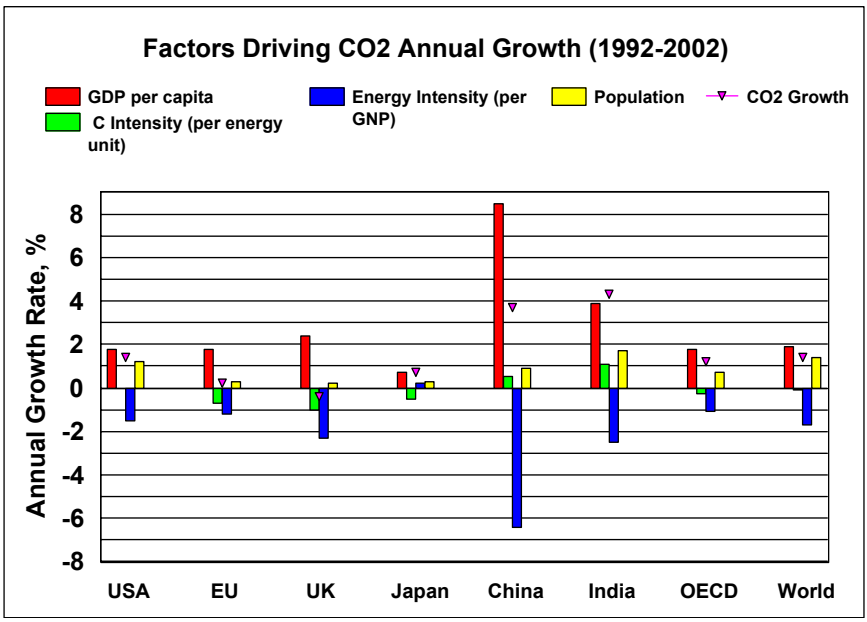

Figure 2: Factors driving CO_2 emissions for selected countries.

If these trends continue, first China and then India will surpass the U.S. as the largest CO_2 emitter in the coming decades. The main driver for this accelerating trend for these populous Asian countries is their expected high rate of economic growth as they strive for a standard of living approaching those of the developed countries.

3 The mitigation challenge; which sectors and gases are most important?

In order to identify the most promising mitigation technologies, it is necessary to understand the current and projected sources of CO_2 and the other greenhouse gases. The author has derived the information in Figure 3 from IEA [4]. This graphic projects world CO_2 emissions by sector; it suggests that power generation and transportation sources will be the fastest growing and will be the key to any successful mitigation program. This IEA baseline scenario, assumes a continuation of CO_2 emission growth consistent with Figure 2: for 2000 to 2030, 1.5%; and for 2030 to 2050, a 2.2% CO_2 growth rates. As mentioned earlier, China and India, with a cumulative population of over 2.4 billion, are projected to continue their rapid economic expansion with commensurate pressure on the power generation and transportation sectors. It should also be noted that the energy transformation category in Figure 3 includes petroleum refining, natural gas and coal conversion to liquids and biomass to alcohols, much of which will feed the transportation sector.

For the U.S., The World Resources Institute [5] has generated a very informative graphic. Figure 4 illustrates the relationship between sectors, end use/activities, greenhouse gases, and the resulting driving force for warming for the year 2000.

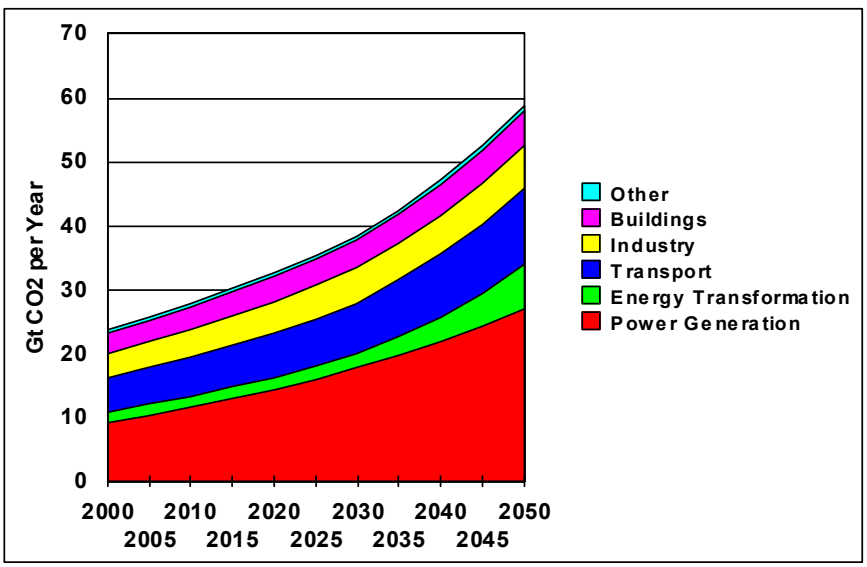

Figure 3: Projected world CO_2 emission growth for key economic sectors.

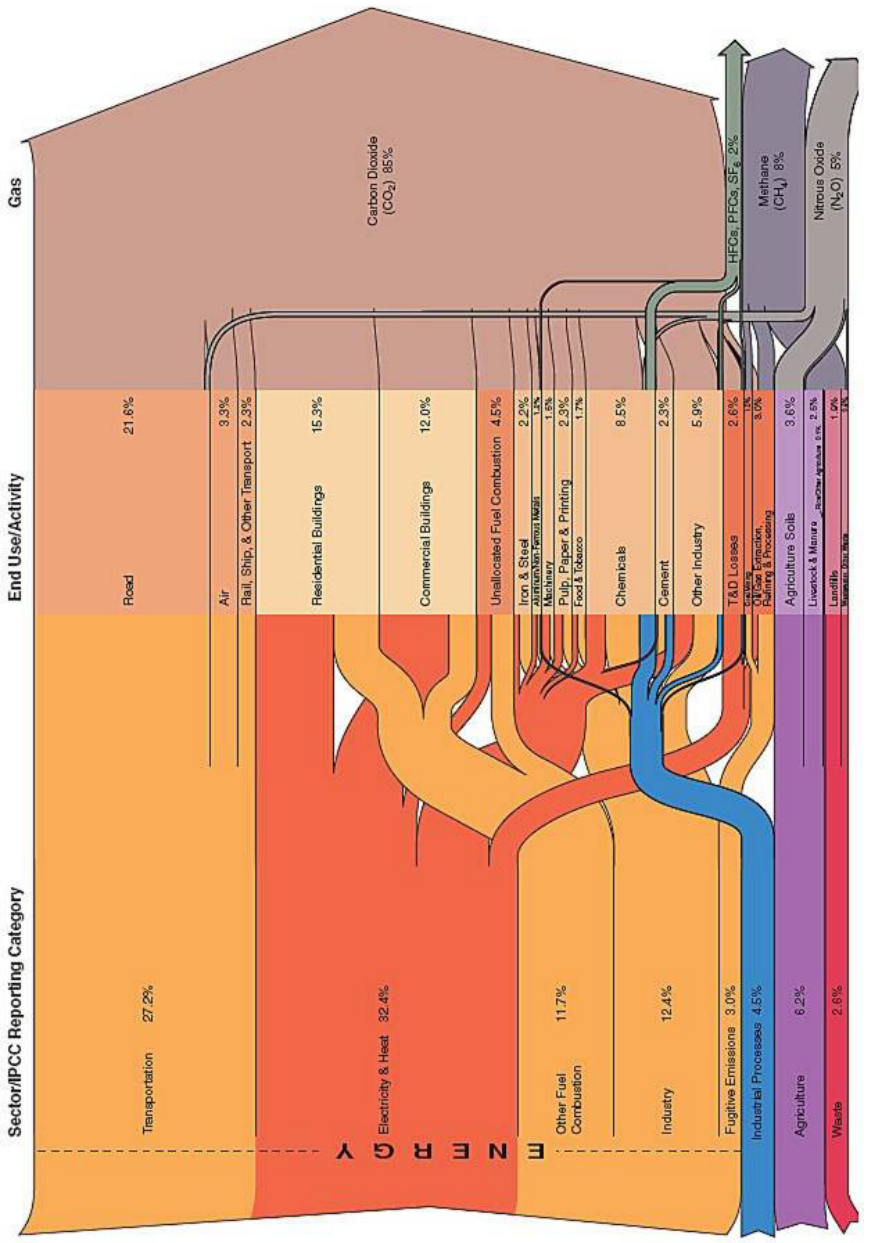

Figure 4: GHG emission flows by sector, end use, and gas in 2000.

This graphic also illustrates the relationship of power generation (electricity and waste heat in the figure), and its end use in the building and industrial sectors.

At this point it should be acknowledged that certain gases other than CO_2 contribute significantly to warming. Figure 4 illustrates this for the U.S. Although CO_2 is the dominant driver, methane and nitrous oxide are significant. For the international view of the relative significance of the key greenhouse gases, the author has generated Figure 5 using the MAGICC model (Wigley and Raper [6]). This figure illustrates the relative thermal forcing of the key greenhouse gases for 2020, 2050, and 2100 using emission projections consistent with the author's modified IEA base case for CO_2 and IPCC [1] Scenario WRE750 for the other greenhouse gases. Note that fine particles show a cooling effect in 2020, which transforms to a warming effect in later years. This is explained since emissions of sulfur dioxide are projected to increase until 2020, whereas the emissions will be reduced later in the century as countries install SO_2 controls. With such emission control, concentrations of sulfate particles, which reflect incoming solar radiation, will consequently be lower, and their cooling effect reduced, yielding warming relative to 1990.

For this paper, *the focus will be on CO_2*, since it is the critical greenhouse gas.

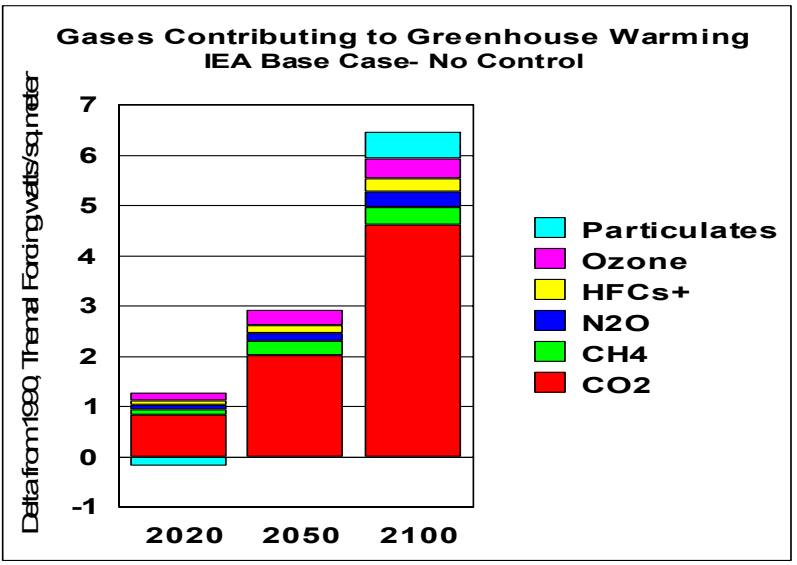

Figure 5: Relative driving force of major greenhouse gases.

4 The mitigation challenge; what role can energy technology play and what are the options:

Although this paper will focus on energy technologies, it should be noted that complimentary approaches could be significant as well. They include life style

changes, such as lowering thermostats in the winter and minimizing driving mileage, and more energy efficient urban planning, which could facilitate mass transit rather than car and truck transport. Also, as suggested by Figure 5, methane, ozone and nitrous oxide mitigation approaches could be significant for the roughly 20% of the thermal forcing associated with them. Finally, there have been various geoengineering approaches suggested which could potentially help buy time until new energy technologies are developed and deployed. For example, Wigley [7] suggested simulating volcanoes, which are known to cool the planet after high altitude eruptions, by purposely emitting large quantities of sulfate particles into the stratosphere. The objective would be to reflect incoming solar radiation. Of course such approaches are very early in their design and would have to be carefully evaluated for their economic and environmental impacts.

In order to understand the potential of various energy technologies to mitigate CO_2 emissions, IEA [4] recently evaluated what it called Accelerated Technology (ACT) scenarios. Of these, the ACT *Map* scenario is the most optimistic, assuming an aggressive and successful R, D & D program to improve commercial or near commercial technologies and a comprehensive demonstration and deployment program for key technologies. It also assumes policies in place that would encourage the use of these technologies in an accelerated time frame. These include CO_2 reduction incentives to encourage low-carbon technologies of cost up to \$25/T CO_2 in all countries from 2030 to 2050. The incentives could take the form of regulation, pricing, tax breaks, voluntary programs, subsidies, or trading schemes.

The author has generated Figure 6, which projects CO_2 emissions by sector, for the ACT Map scenario, based on their assumption that major technology implementation starts in 2030. Figure 7 depicts the CO_2 savings projected by sector using the ACT Map scenario. Most of the savings relate to the power generation sector, which includes both production and end use savings. This IEA scenario is projected to result in the mitigation of 32.5 Gt of CO_2 in 2050. As will be discussed subsequently, this level of mitigation, would be impossible without the use of improved and in some cases breakthrough energy technologies. Such technologies are necessary for both energy production, i.e., power generation, and to enhance end use efficiency, i.e., lower emission vehicles.

It is important to note that for the IEA Map scenario extended to 2100, the author's MAGICC (Wigley and Raper [6]) calculations indicate best-guess CO_2 concentrations in 2100 of 500 ppm and a corresponding warming of 2.0^{o}C relative to 1990. This is despite the IEA assumption of an aggressive R,D&D and deployment program and the author optimistically assuming further major (2% per year) emission reductions for 50 years beyond the IEA time frame of 2050. This suggests that even a major mitigation program, globally implemented, based on successful development and deployment of several new technologies, will still allow substantial global warming in 2100.

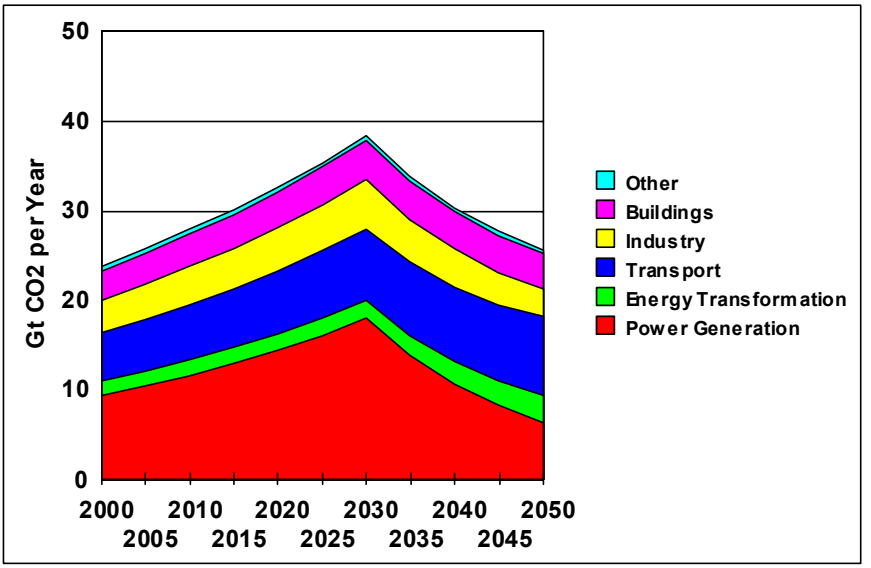

Figure 6: Sector CO_2 emissions for the IEA ACT scenario.

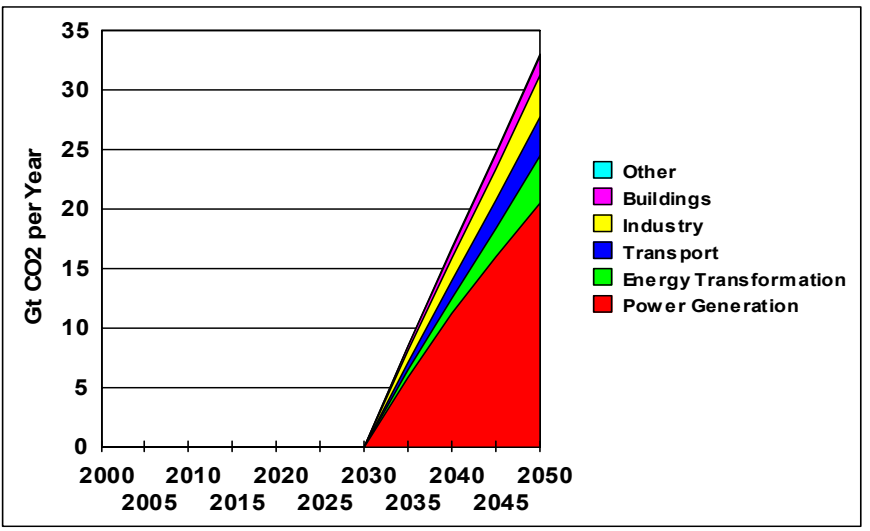

Figure 7: CO_2 emission reductions per sector for the ACT scenario.

The author has generated Tables 1–4 for the key four sectors to summarize the potential and status of key technologies based on the following recent energy technology assessments: IEA [4], Hawksworth [8], Pacala and Socolow [9], Morgan et al. [10]. Two additional references contained useful information relative to hydrogen/fuel cells, USEPA [11], and nuclear technologies, USEPA [12].

Let us now focus on these four critical sectors and examine the technology options available, their current state of the art, and the required R, D&D to allow the technology options to meet their potential to reduce CO_2 emissions.

5 Power generation sector

Of all the sectors, the power generation sector, which is projected to grow at an annual rate of 2%, has the greatest potential to reduce CO_2 emissions in the coming decades. However, it should be noted that there are major capacity expansions underway for coal-fired power generation in China, India, and other countries. Since such plants have no CO_2 mitigation technology planned and can have lifetimes up to 50 years, the sooner technology is ready for implementation and mandated, the sooner new plants can incorporate such technology and control emissions. Carbon dioxide retrofit technology is theoretically possible, but such technology will not be commercially available for some time and will likely be substantially more expensive per unit of power generated than would be the case for new plants.

Major reductions can result from lower emissions on the generation side and as a result of lower usage via enhanced end use efficiency. Table 1 presents a summary of major generation options that offer significant opportunities for CO_2 mitigation. They are presented in the order of highest potential for CO_2 mitigation consistent with the IEA ACT Map scenario. Included in this and the subsequent tables are the IEA projected CO_2 savings for each technology in Gt of CO_2 in 2050. To put these numbers in perspective, full implementation of the IEA Map scenario would mitigate 32.5 Gt of CO_2.

Key generation technologies include nuclear power, natural gas/combined cycle, and three coal combustion technologies (IGCC, pulverized coal/oxygen combustion, and conventional pulverized coal), all with integrated CO_2 capture and underground storage. With the exception of wind power, renewable technologies (green font in Table 1) are not projected to have major mitigation impacts in the 2050 time frame. In the case of solar generation, the technology is projected to be prohibitively expensive unless there is a major research breakthrough. For biomass, major utilization is projected to be limited by its dispersed nature, its low energy density, and competition for the limited resource in the transportation sector.

The author rates R,D&D needs in the power generation sector particularly critical, especially in the area of CO_2 capture and storage (CCS) and for the next generation of nuclear power plants. The CCS area is in the early developmental stage, with extraordinary potential, but with a host of questions that can only be resolved through a major program with a particular focus on demonstrations for the key geological formations, most applicable to the greatest potential capacity. For advanced nuclear power, the technology is quite promising and could start making a major impact by 2030. However, technology needs a number of successful demonstrations to allow for resolution of remaining technical problems and to instill confidence in the utility industry that the technology is affordable and reliable, and in the public, that it is safe.

Table 1: Key technologies for CO_2 avoidance from power generation (projected impact in Gt/Yr of CO_2).

Technology	Current State of the Art	2050 Impact	Issues	R,D&D Needs	Other Potential Environmental Impacts
Nuclear Power-next generation	Developmental, Generation III+ and IV: e.g. Pebble Bed Modular Reactor and Supercritical Water Cooled Reactor	1.9	Deployment targeted by 2030 with a focus on lower cost, minimal waste,enhanced safety and resistance to proliferation	**High**, Demonstrations of key technologies with complimentary research on important issues	Reduction in emissions of SOx, NOx, Fine PM; small but potent and long-lived waste, could contaminate small area
Nuclear Power-current generation	Commercial, Pressurized Water Reactors and Boiling Water Reactors (Generation III)	1.8	Plant siting, high capital costs, levelized cost 10 to 40% higher than coal or gas plants, potential U shortages, safety, waste disposal and proliferation	**Medium,** Waste disposal research	Reduction in emissions of SOx, NOx, Fine PM; small but potent and long-lived waste, could contaminate small area
Natural Gas Combined Cycle	Commercial, 60% efficiency	1.6	Limited by natural gas availability, which is major constraint; high effiency & low capital costs, extraction R&D coud enhance availability of CH4	**Medium**, higher efficiencies with new materials desirable	Reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and residues
Wind Power (renewable)	Commercial	1.3	Costs very dependent on strength of wind source, large turbines visually obtrusive, intermittent power source	**Medium**, higher efficiencies, on-shore demonstrations	Reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and residues
Coal IGCC with CO2 Capture and Underground Storage	*IGCC* : early commercialization , Underground storage *(US)* : early development.	1.3	*IGCC* :High capital costs, questionable for low rank coals,complexity and potential reliability concerns; *US* : Cost, safety, efficacy	**High**, *IGCC* : Demos on a variety of coals, hot gas cleanup research; *US* : major program with long term demos evaluating large number of geological formations to evaluate efficacy, cost and safety	Lower power plant efficiency yields greater emissions of SOx, NOx, Fine PM
Pulverized Coal/Oxy combustion with CO2 Capture and Storage	Developmental	1.3	Oxygen combustion allows lower cost CO2 scrubbing, but oxygen production cost is high; *US* : Cost, safety and permanency	**High**, large pilot followed by full scale demos needed, low cost O_2 production needed, *US* requires major program (see write-up above)	Lower power plant efficiency yields greater emissions of SOx, NOx, Fine PM
Pulverized Coal with CO2 Capture and Storage	Underground storage developmental; CO2 scrubbing with MEA near commercial but too expensive	1.3	*US* : Cost, safety and efficacy issues, CO_2 scrubbing energy intensive: yielding unacceptable costs	**High,** *US* requires major program (see write-up above); affordable CO_2 removal technologies need to be developed and demonstrated	Lower power plant efficieny yields greater emissions of SOx, NOx, Fine PM
Solar-Photovoltaic and concentrating (renewable)	First generation commercial, but very high costs	0.5	Costs unacceptably high, solar resource intermittent in many locations	**High**, breakthrough R,D&D needed to develop & demo cells with higher efficiency and lower capital costs	Reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and residues
Biomass as fuel and co-fired with coal (renewable)	Commercial, steam cycles	0.5	Biomass dispersed source, limited to 20% when co-fired with coal	**Medium,** biomass/IGCC would enhance efficiency and CO_2 benefit; also genetic engineering to enhance biomass plantations	Reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and Residues for disposal or use; however potential eco impacts from biomass plantations
Hydroelectric (renewable)	Commercial	0.5	Capital costs high, potential ecological disruption, siting challenges	**Medium**, minimize environmental footprint	Ecosystem Impacts
More Efficient Coal Fired Power Plants	Early commercialization of supercritical and ultra supercritical	0.2	Currently maximum efficiency of 45% , yielding 36% less CO_2 than current fleet	**High,** new affordable materials needed to enhance efficiency to 50 to 55%	Small reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and residues
Coal IGCC with no CO2 Capture and Storage	IGCC: early commercialization	0.2	IGCC: High capital costs, complexity and reliability concerns, only modest CO2 savings without CCS	**High**, Demos on a variety of coals, hot gas cleanup research	Small reduction in emissions of SOx, NOx, Fine PM; fewer mining impacts and residues

6 Building sector

The building sector utilizes large quantities of electricity and fossil fuels and is expected to increase CO_2 emissions for the next several decades at about 1.1% per year. Figure 4 illustrates the importance of this sector in the US, with commercial and residential buildings contributing 27.3% to national greenhouse gas emissions via use of electricity and direct use of fossil fuels, mostly natural gas and oil. Table 2 summarizes major technologies capable of achieving significant reductions in CO_2 generation in the 2050 time frame. The technologies are divided into two categories: (1) heating and cooling and (2) appliances, which include lighting.

Table 2: Key technologies for CO_2 avoidance from buildings (projected impact in Gt/year of CO_2).

	Technology	Current State of the Art	2050 Impact	Issues	R,D&D priority and Needs	Other Potential Environmental Impacts
Heating & Cooling	**High efficiency building envelope: insulation, sealants, windows**	Commercial	1.6	Lack of incentive, high initial costs, long building lifetime	**Low/medium priority**, incremental improvements to lower cost and enhance performance	Reduction in coal & natural gas emissions
	High efficiency building heating and cooling	Commercial	1.1	Lack of incentive, high initial costs	**Low/medium priority**, incremental improvements to lower cost and enhance performance	Reduction in coal & natural gas emissions
	Solar heating and cooling	First generation commercial	0.6	High initial costs, availability of low cost efficient biomass heating systems	**Medium**, focus on development of advanced biomass stoves and solar heating technology in developing countries	Reduction in coal & natural gas emissions
	District Heating and cooling	Commercial	0.5	Intial capital costs high, CO2 benefit variable; limited applicability	**Low/medium**, improve economics for lower population densities and optimize system to include cooling option	Reduction in coal & natural gas emissions
	Building energy management	First generation commercial	0.2	Computer technology not being adequately applied; lack of incentive & knowledge	**Medium**, integration and operation research and tie in with emergency demand response measures	Reduction in coal & natural gas emissions
Appliances	**More efficient Electric appliances**	Commercial	2.1	Higher initial costs and lack of information to the consumer	**Low/medium priority**, incremental improvements to lower cost and enhance performance	Reduction in coal & gas emissions: SOx, NOx and PM and residues
	More efficient lighting systems	Commercial-fluorescent	1.0	Lack of incentive given higher initial costs	**Medium**, LED and OLED technology need further development with aim of lowering initial cost	Reduction in coal & gas emissions: SOx, NOx, PM and residues
	Reduce stand-by losses from appliances, computer peripherals, etc.	Commercial	0.3	Lack of incentive from vendors and lack of knowledge from end-users	**Low**	Reduction in coal emissions: SOx, NOx and PM and residues

For each of the two categories, the technologies are listed in order of their potential impact in 2050 according to IEA. The technologies summarized in blue font are aimed at enhancing end use efficiency, whereas the rest deal with new alternative building heating/cooling technologies. It is important to note, that high-efficiency appliances and heating and cooling technologies are currently commercial. Lack of incentive and higher initial costs are the primary reasons for the slow rate of utilization. This is in contrast to the power generation sector, which is constrained by unavailable or undemonstrated technology.

7 Transportation sector

The transportation sector is growing at a fast rate, estimated at 2% per year between 2003 and 2050, driven by developing countries such as China and India, with a combined population of 2.3 billion or 37% of the world's population. It is second only to the power generation sector in importance for the foreseeable future. There are two major technology categories: vehicles and fuels. Technology is currently commercially available for major reductions in CO_2 emissions per mile traveled, especially for light-duty vehicles. Table 3 summarizes the status of major technologies. The first two rows illustrate that major CO_2 reductions could be achieved by incorporating the most efficient internal combustion, chassis, A/C and tire components. Also, hybrid technology, if optimized for efficiency and utilized with high-efficiency chassis components, can have a substantial positive impact. The main impediment to more robust utilization of these commercially available technologies appears to be higher initial costs for hybrids and buyer preferences that, in North America and more recently in Europe, are for larger, heavier, less-efficient vehicles.

IEA [4] projected that increasing and substantial quantities of CO_2 will be emitted by gas and coal to liquid processes, in the energy transformation sector.

The author believes that processes generating liquid fuels from tar sands and oil shale could be major emitters as well. To the extent vehicle efficiency can be improved and renewable fuel options developed, major savings can be realized in the transformation sector.

Of all the biomass processes, thermo-chemical processes that can convert biomass to bio-diesel or other transportation fuels using gasification, pyrolysis, or Fischer-Tropsch technology, appear to have the most potential for CO_2 mitigation and should be considered for an aggressive R, D & D program.

Also, ethanol production by biochemical processing of biomass offers the potential for large-scale displacement of gasoline. However, breakthroughs will be necessary in the ability to chemically break down major biomass components to sugar for fermentation to produce ethanol.

Hydrogen/fuel cell vehicle technology is still in the early development stage, since the fuel cell stack still has limitations in terms of cost and longevity, and hydrogen storage in vehicles remains problematical. Also, EPA [10] and IEA [4] assessments suggest that CO_2 savings would not be substantial unless or until the hydrogen could be generated from low-emission, renewable sources.

Table 3: Candidate technologies for CO_2 avoidance from mobile sources (projected impact in Gt/year of CO_2).

	Technology	Current State of the Art	2050 Impact	Issues	R,D&D Needs	Other Potential Environmental Impacts
Vehicles	**Improvements: Current Internal combustion engine components**	First generation: commercial	2.2	Lack of customer incentive major problem; trend to larger vehicles in US and recently Europe counter-productive	**Medium**; Transmission and drive train improvements	Lower emissions of VOCs and Nox
	Non-engine Improvements:tires, A/C, light materials	First generation: commercial	1.8	Lack of customer incentive major problem; trend to larger vehicles in US and Recently Europe counter-productive	**Medium**, Lower weight construction, improved tires and more efficient A/Cs	Lower emissions of VOCs and Nox
	Hybrid vehicles	First generation: commercial	1.4	Higher costs (about $3000),"light" hybrids not as efficient as full hybrids, some newer models yield power over mileage benefits	**Medium/High**,Minimize incremental cost and enhance efficiency	Lower emissions of VOCs and NOx
	Hydrogen fuel cell vehicles	Developmental	0	Fuel cell costs and fuel cell stack life; also hydrogen storage, safety and lack of infrastructure	**High**, Breakthrough R,D&D needed to develop cost competitive, long lived fuel cells. Vehicle storage R,D&D also needed	On road emissions close to zero, H2 production emissions depends on feedstock & process
Fuels	**Ehanol from sugar**	Commercial	0.7	Limited by land capable of high sugar yields,e.g., sugar cane	**Medium**, develop sugar cane cultivars with higher yield and more frost tolerant	Potential eco impacts from biomass plantations, other impacts unclear, environmental studies would be useful
	Biodiesel & other fuels from biomass; thermochemical processes	Developmental	0.6	Developmental,yet potentially high production and lower cost via gasification/Fischer-Tropsch synthesis	**High,** Breakthrough R,D&D needed to develop and demonstrate viable technology for biomass feedstock	Potential eco impacts from biomass plantations, other impacts unclear, environmental studies would be useful
	Biodiesel from vegetable oil	First generation: commercial	0.2	High costs, low yield from oil crops, limited waste cooking oils, low S a plus	**Low**	Not clear, environmental characterization would be useful
	Ethanol from grain/starch,e.g., corn	Commercial	0.2	Limited by grain supply; high costs, energy intensive production	**Low**	Modest delta impacts compared to base case
	Ethanol from biomass; biochemical process	Early Developmental	0	Inability to convert all biomass components, high production costs, dispersed biomass source	**High**, Breakthrough R,D&D needed to develop lower cost generally applicable process(es)	Not clear, environmental characterization would be useful
	Hydrogen	Commercial from natural gas and electricity	0	Cost via electrolysis high, CO2 benefits if produced via natural gas low	**High;** breakthrough research to generate H2 at low cost from renewable or nuclear sources	Depends upon feedstock source and production process

Despite the serious technical issues, in light of the ultimate potential of fuel cell /hydrogen and biochemical ethanol, the author believes both are also strong candidates for an aggressive R, D, & D focus with the aim of breakthrough technology.

8 Industrial sector

CO_2 emissions from the industrial sector are projected to grow at an annual rate of 0.7% per year over the next several decades. Table 4 summarizes major technologies applicable to this sector. Although CO_2 emission control can be specific to a particular industry, there are a number of technologies that can be

Table 4: Candidate technologies for CO_2 avoidance from industrial sources (impact in Gt/year of CO_2).

Technology	Current State of the Art	2050 Impact	Issues	R,D&D Needs	Other Potential Environmental Impacts
Motor Systems	Commercial	1.5	For most industries not a major cost; lack of expertise for some industries	**Medium**; lower costs and higher efficiencies desirable	Reduction in coal emissions: SOx, NOx; and PM and residues
CO2 Capture and Storage	Early development	1.5	Applicability limited to large energy-intensive industries; key questions:cost, safety, efficacy	High, major program with long term demos evaluating large number of geological formations to evaluate efficacy, cost and safety	Lower power plant efficieny yields greater emissions of SOx, NOx, Fine PM
Fuel Substitution in Basic Materials Production	Commercial	0.5	Natural gas substiution for oil and coal can be expensive	**Low**	Unclear, environmental studies useful
Enhanced energy efficiency: existing basic material processes	Commercial	0.4	Developing countries can have low energy efficiency due to lack of incentive and/or expertise	**Low**	Unclear, environmental studies useful
Feedstock Substitution in key industries	Commercial	0.4	Biomass and biopastics can substitute for petroleum feedstocks and products; however cost high & availability low	**Medium**, develop affordable substitute feedstocks and products based on biomass	Unclear, environmental studies useful, depends on feedstock & process
Steam systems (required for many industries)	Commercial	0.3	For most industries not a major cost; lack of expertise for some industries	**Low**	Reduction in coal emissions: SOx, NOx and PM and residues
Materials/Product Efficiency	First generation: commercial	0.3	Little incentive to minimize the CO2 "content" of materials and products; life cycle analyses required	**Medium,** conduct life cycle analyses of key materials and products with the aim of minimizing CO2 "content"	Potential reduction in air emissions, water effluents and wastes, depenging on substitute material
Cogeneration (combined heat and power)	Commercial	0.3	Limited by electric grid access that would allow the ability to feed electricity back to grid, also high capital costs	**Low**	Reduction in coal emissions: SOx, NOx and PM and residues
Enhanced energy efficiency: new basic material processes	Development al to Near-commercial depending on industry	0.2	New, innovative production processes require major R,D&D and would need reasonble payback to replace more C intensive processes	**Medium/High**, Develop and demonstrate less carbon intensive production processes for key industries	Potential reduction in air emissions, water effluents and wastes, depending on new process

applied to a large fraction of the industrial sector (blue font in Table 4). Generally applicable technologies include: more efficient motors and steam generators and enhanced use of cogeneration technology; all are commercially available and offer the potential for major reductions. For the larger, more energy intensive industries such as cement kilns, ammonia production, and blast furnaces, CO_2 capture and storage also offers potential for mitigating large quantities of CO_2. However, as mentioned earlier, CCS is in the early developmental stage with a host of questions that can only be resolved through a major program with a particular focus on demonstrations for key geological formations.

Developing and deploying new or modified industrial production processes can also yield important CO_2 emission mitigation potential. Processes can be modified to utilize more environmentally-friendly feedstocks, or fundamentally new basic material processes can be introduced with inherently less energy

Another approach that has potential is to encourage utilization of products which have lower CO_2 "content," i.e., require less carbon intensive energy during the their production, use, and disposal. These could be considered "climate-friendly" products. There is currently no incentive to use such products. Also, comprehensive life cycle analyses would be necessary to quantify product CO_2 "content".

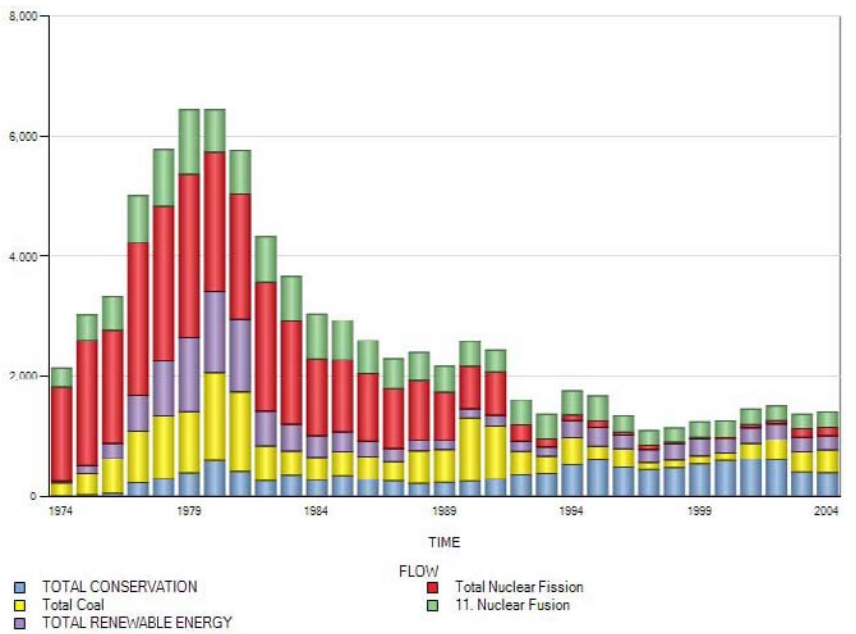

Figure 8: U.S. Federal R, D, &D expenditures for key energy sectors, 2004 $.

9 Adequacy of R, D, &D

IEA [4], Hawksworth [8], Morgan et al. [10], and the author nine years ago (Princiotta [13]) have observed that R, D, & D funding in the energy area will need to be substantially increased in order for key technologies to be ready to reduce carbon dioxide emissions in a time frame consistent with an aggressive mitigation program. Most recently, The Stern Report [14] concluded: "…support for energy R&D should at least double, and support for the deployment of new low-carbon technologies should increase up to five-fold."

Figures 8 and 9, generated from IEA [15], depict U.S. and world research expenditures in critical areas: nuclear power, coal, conservation, and renewables. (Note that world expenditures have only been compiled since 1992.) As can be seen, in the U.S., there has been a major *decrease* in funding since the 1980s, with no major increases in recent years. It is also noteworthy that Europe and Japan have been much more active in the nuclear research area, whereas the U.S. is the key player in coal-related research.

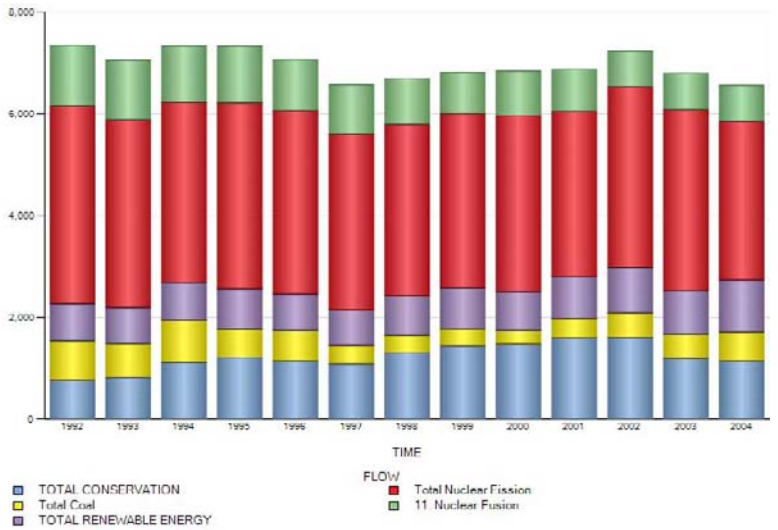

Figure 9: World R, D, & D expenditures for key energy sectors, 2004 $.

It should be recognized that in the last few years, the U.S. has redirected some of its research resources to some key technologies, especially: hydrogen/fuel cells, IGCC, carbon capture and storage, and most recently biomass to ethanol technologies. The U.S. has coordinated its efforts in this area through the Climate Change Technology Program, CCTP [16]. Within the constraint of current budget priorities, the CCTP has coordinated a diversified portfolio of advanced technology R & D, focusing on: energy-efficiency enhancements; low-GHG-emission energy supply technologies; carbon capture, storage, and sequestration methods; and technologies to reduce emissions of non-CO_2 gases.

This could provide a foundation for an expanded program, with funding and schedules consistent with an aggressive mitigation program. Also, the USEPA [17] is implementing a series of voluntary programs which encourage greenhouse gas reduction. They include: Energy Star for the building sector, transportation programs and non-CO_2 emission reduction programs in collaboration with industry.

It is important to note, that IGCC and most of the other non-coal technologies offer the potential for lower air emissions, water effluents and waste generation residues. Also, note that the transportation technologies all offer the potential for reducing our dependency on foreign oil. Further, the country or countries that can bring these technologies to market first, has/have the potential for major revenue streams from what could be a huge international market.

10 Summary and conclusions

The key energy sectors are power generation, transportation, industrial production, and buildings. The power sector and transportation sectors are particularly important, since they are projected to grow at relatively high rates, with China and India being key drivers.

The power generation sector, projected to grow from a large base at 2% annually, offers the greatest opportunity for CO_2 reductions. However, since the key source of emissions is coal combustion, it is critically important to develop affordable CO_2 mitigation technologies for such sources. CCS offer the potential to allow coal use while at the same time mitigating CO_2 emissions. These technologies could be applied to current pulverized coal (PC) boilers, but current CO_2 scrubbing technology is too energy intensive and expensive for PC conditions. Therefore, alternatives to PC boilers are important. The two major candidates are IGCC and oxygen-fed combustors, both of which can remove CO_2 more affordably for ultimate sequestration. However, CCS is an unproven technology with many serious cost, efficacy, and safety issues. Nuclear power plants, natural gas/combined cycle plants, and wind turbines all have the potential to make significant contributions.

The building sector is where much of the electricity generated is utilized and where there are many currently available technologies that can significantly reduce the use of electricity and other energy sources, with a corresponding decrease in CO_2 emissions. The constraints here are less technological and more socioeconomic. However, to the extent R & D can lower cost and raise efficiency of building components, it can help provide extra incentive for building owners to invest in the most efficient heating and cooling systems, lighting, and appliances.

The transportation sector is growing at a rate of 2% per year. The challenge in this sector is two-fold. The first challenge is that current propulsion systems all depend on fossil fuels with their associated CO_2 emissions, suggesting that technologies based on renewable sources such as biomass would be important. The second challenge is that the automobile industry, driven by consumer preferences (especially in North America), have offered heavy, inefficient

vehicles such as SUVs. A review of developing technologies suggests that hybrid vehicles and biomass-to-diesel fuel via thermochemical processing are the most promising. However, cellulosic biomass-to-ethanol and hydrogen/fuel cell vehicles offer longer term potential if key technical issues are resolved and, in the case of hydrogen, renewable sources are developed.

Industrial sector emissions are projected to grow at an annual rate of 0.7%. Although CO_2 emission controls can be specific to a particular industry, the following key commercial technologies can be applied to a large fraction of the industrial sector: efficient motors, steam generators, and enhanced use of cogeneration technology. For the larger, more energy-intensive industries, such as blast furnaces, CO_2 capture and storage offer the potential for mitigating large quantities of CO_2. Developing and deploying new or modified industrial production processes can also yield important CO_2 emission mitigation potential. Another attractive approach is to encourage utilization of products that have a lower CO_2 content," i.e., require less carbon intensive energy during product production, use, and disposal.

If mitigation consistent with the IEA scenario is to be accomplished, a major increase in R&D resources will be needed. Technology research, development, and demonstration are of particular importance for coal generation technologies: IGCC, oxygen coal combustion, and CO_2 capture technology for pulverized coal combustors. All of these technologies will have to be integrated with underground storage, a potentially breakthrough technology, but one which is an early stage of development. Also important are next generation nuclear power plants, biomass to diesel fuel processes, cellulosic biomass-to-ethanol production technology, and hydrogen production technology.

Availability of key technologies will be necessary but not sufficient to limit CO_2 emissions. Since many of these technologies have higher costs and/or greater operational uncertainties than currently available carbon intensive technologies, robust policies will be necessary to encourage their utilization.

Finally, given the challenge and uncertainties associated with an aggressive mitigation program based in part on unproven, developmental technologies, it may be prudent to consider all available and emerging technologies. This suggests that fundamental research on energy technologies *in addition* to those in Tables 1 to 4, be part of the global research portfolio, since breakthroughs on today's embryonic technologies could yield tomorrow's alternatives. Also, it may also be prudent to consider geoengineering options, which although radical in concept, could potentially buy the time needed to make the necessary adjustments in our energy and industrial infrastructure consistent with an aggressive mitigation program. For example, it is suggested that the simulated volcano option proposed by Wigley [7] be seriously evaluated.

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CDM project approval and evaluation criteria: comparative study of Morocco and South Africa

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Abstract

Since the coming into force of the Kyoto Protocol (KP) in February 2005, the flexible Clean Development Mechanism (CDM) has gained momentum and much recognition in many developing countries globally. Africa, and specifically Morocco and South Africa are part of this band wagon. This paper critically reviews the CDM approval and evaluation criteria for Morocco and South Africa with the view of determining possible future competition points in attracting CDM foreign direct investment in these countries. The paper also serves as a reference point for other developing countries that have or are contemplating implementing CDM project approval and evaluation criteria. The paper shows significant differences in approval time frames and sustainable development criteria. It takes about 42 days in Morocco for proponents to get responses on their proposed CDM projects compared to 60 days (if initial voluntary screening is excluded) and 90 days (if initial voluntary screening is included) in South Africa. Also sustainable development criteria appears to be more stringent for South Africa compared to that of Morocco. By the time of writing this paper, 60 CDM project proposals had been submitted and were at various approval stages in Morocco compared to 20 in South Africa.
Keywords: CDM project approval criteria, Morocco, South Africa.

1 Introduction

Apart from the traditional determinants of foreign direct investment (FDI), two of the most recent key determinants for attracting CDM project-related FDI by host countries are the CDM project approval and evaluation criteria. Based on

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this assumption, this paper compares these criteria between two African countries namely: Morocco and South Africa. Already, the global spread of CDM project investment Ellis *et al* [1] depicts a picture of severe imbalances with Korea accounting for 27%, India (16%), Brazil (11%), China (9%), other Latin American countries (17%), other Asian countries (18%), Africa (5%), Europe (1%) and none for the Middle East. Such comparison assists in developing competitive environments for attracting CDM projects. Geographically, Morocco and South Africa are countries located in the far North and far South of the African continent respectively. The CDM permits developed countries to invest in projects that reduce green house gases (GHGs) in developing countries and earn *carbon credits or carbon offsets* Nhamo [2]. The Kyoto Protocol, which entered into force in February 2005, compels developed countries to reduce collectively GHGs by an average of 5.2% between the period 2008–2012 based on the 1990 levels United Nations [3].

2 Generic CDM project cycle

There is a series of steps that are involved in CDM project cycle. The key ones include (a) the preparation of the Project Design Document (PDD), (b) Validation and Approval, (c) Registration, (d) Monitoring, (e) Verification and Certification, and (f) Certification and Issuance of the Certified Emission Reductions - CERs). Details concerning these and other stages are presented in table 1.

It is from the above generic CDM project cycle that host countries are given the jurisdiction to develop their own and similar CDM approval and evaluation criteria. The Kyoto Protocol (KP) requires that each host country designate a national authority for the CDM [4]. The Designated National Authority (DNA) as it is known is the legal entity or institution designated by the host country to manage the CDM project implementation processes. Given that one of the Protocol's two key goals is to assist developing countries that host CDM projects to achieve sustainable development, a key and early function of the DNA is to develop 'sustainability criteria' that will be used by the DNA to judge whether a proposed CDM project will contribute to the sustainable development of the country. If such a finding is made, then the project should receive the approval of the host country. This approval is a prerequisite for a CDM project and a factor that investors consider, often waiting for the DNA to indicate its support for a project before deciding whether to invest in it or not.

3 CDM national structures

The CDM project approval and evaluation criteria for Morocco is laid out in the 2004 CDM Strategy, Organisation and Procedures document Ministry of Land-use Management, Water and the Environment [5]. Morocco ratified the KP in September 2002 [5] and South Africa did likewise two months earlier in July 2002 Mqadi *et al* [6]. The Ministry of Land-use Management has been assigned as the DNA for CDM. In terms of the requirement that CDM projects must fulfil sustainable development requirements, Morocco has prioritised six key CDM

project areas with promising potential for improving socio-economic and environmental situations namely: renewable energy development; energy efficiency development; better organised transport system resulting in higher energy performance and lower pollution impacts; healthier waste management; as well as forestation and reforestation.

Table 1: Generic stages in CDM project cycle.

Stage	Description	Responsibility
Host country approval	Approval at the national level by the Designated National Authority (DNA), consistent with domestic laws and political priorities.	Project developer
Project Design Document	Identification of a concept and development of the project design documents such as baseline estimate, additionality, sustainable development contributions, monitoring and verification plan and stakeholders' opinion.	Project developer or participants
Validation and Approval	Third party validation of baselines and other details to confirm that CERs as claimed by the project are considered realistic. Approval is when the DNA of each party involved confirm their voluntary participation and the DNA of the host country attest that such CDM project contributes to the sustainable development of the country	Designated Operation Entity (DOE) Designated National Authority
Registration	Registration of the project activity with the CDM Executive Board, once the project has received host country approval.	CDM Executive Board on demand of DOE
Financing	Investor providing capital in the form of debt or equity; investors may/ may not be carbon buyers.	Project developer
Implementation	Building, commissioning and initiating operations.	Project developer
Monitoring	During commissioning and further operations, the progress and GHG offsets are to be monitored.	Project developer
Verification	Independent assessment of project performance against the validated design.	DOE
Certification and issuance of CERs	Based on the verification report, the CDM Executive Board certifies and issues CERs.	Executive Board

[Source: Lee *et al* [4]]

For South Africa, national CDM structures are documented in the Regulations for the Establishment of a DNA for the CDM of 22 July 2005 Republic of South Africa [7]. From the Regulations, the Director-General of the national Department of Minerals and Energy has been designated as the DNA and according to Article 2(2) of the regulations shall perform all powers and duties of the DNA. This includes delegating any such power to execute the DNA's duties. What is of interest here is that the DNA does not stand out as a separate new authority but is integral to the day to day duties of the Director-General. This is a similar orientation to that of Morocco. In consultation with the Steering Committee, the DNA shall: (a) establish and apply a CDM project approval procedure, (b) evaluate CDM projects, (c) issue letters of approval, (d) facilitate effective participation by key stakeholders in the approval process of CDM projects, (e) promote CDM projects in the country, (f) monitor and report to the Minister of Minerals and Energy CDM activities and (g) deal with all donations

for CDM as per the requirements of the Public Finance Management Act of 1999. Details regarding CDM project implementation national structures and procedures for both countries are summarised in table 2.

Table 2: National structures and procedures for CDM.

Attribute	Morocco	South Africa
Institutions	CDM DNA – encompassing the CDM National Council and Permanent Secretariat of the CDM National Council	DNA for CDM – encompassing the Director General for the Department of Minerals and Energy, Steering Committee (SC) for the DNA and Expert Advisory Committee.
Capacity building	Done to economic operators and the CDM National Council	Done to key stakeholders at National and Provincial scales
Internationally promoting of CDM in Morocco	Contact with potential CDM investors, carbon buying organisations and Annex I Parties; Website created at: www.mdpmaroc.com	DNA specifies one of its key mandates as promoting South Africa as a suitable and attractive investment opportunity for CDM project developers and overseas investors; Special website established at: http://www.dme.gov.za/dna/index.stm
Monitoring international CDM negotiations	Follow-up activities with the CDM Executive Board and discuss these during KP Conference of Parties; Follow-up on international publications on CDM projects	Not clearly spelt out
CDM National Council/Steering Committee	CDM National Council comprises the President of National Council and 20 high level representatives including those from 10 ministries	Steering Committee comprised of a Chair from the DNA and 9 national departments

The main difference between the two countries is that Morocco has more formalised procedures, especially regarding international promotions, lobbying and monitoring for CDM investment. The procedures also include a wider range of stakeholders in the CDM National Council compared to South Africa's Steering Committee that holds the same functions. However, the CDM National Council and the Steering Committee have similar roles, particularly those pertaining to the review and assessment of projects submitted for CDM to respective DNAs, development and approval of sustainable development criteria, Ministry of Land-use Management, Water and Environment; Republic of South Africa [5,7]. In addition, both these institutes were established in 2004.

4 CDM project evaluation and approval procedures

Morocco starts by acknowledging that one of the criteria that attracts a country to invest in CDM is the functioning of their DNA. Hence the more project endorsement process is clear, transparent and quick, the more investors will be prepared to initiate CDM projects Ministry of Land-use Management, Water and Environment [5]. The evaluation and approval criteria for both countries are similar in many respects (table 3) although Morocco appears to have much more streamlined procedures.

Table 3: CDM project evaluation and approval procedures.

Attribute	Morocco	South Africa
Preliminary evaluation	CDM Morocco Project Idea Note (PIN) submitted – to check whether it leads to real and measurable GHG reductions; conforms to the national sustainable development criteria; and has no external negative effects. All this takes a maximum of 14 days.	Initial (voluntary) screening done with developer submitting the Project Identification (PIN) and application form that is reviewed resulting in (a) a Letter of No-Objection (leading to final submission) or (b) Letter of Objection and comments leading to a complete rejection or the revision of PIN and ultimate final submission. All this takes 30 days.
In-depth evaluation	In-depth review of data and project components with regard to set international and national sustainable development criteria. Project Design Document (PDD) submitted by the promoter. EIA required as per the national regulations. All this takes a maximum of 28 days.	Developer submits PDD (inclusive of EIA) to the DNA. PDD made available online for public comments for 30 days whilst it simultaneously undergoes review by the DNA. Decision made by the DNA to either approve (leading to the issuance of the Letter of Approval) or reject (with reasons) leaving the developer with an option to appeal to the Minister of Minerals and Energy. Appeal to be made within 60 days, the same amount of time it takes to have a decision made on the submitted PDD. Overall, either a 60 or 90 days CDM project approval process is in place.
Sustainable development criteria	CDM projects must contribute to: the mitigation of global carbon cycle; sustainability of the local environment; creation of employment; durability of payments; macro-economic plan; effect on costs; technology autonomy and sustainable use of natural resources.	Three broad criteria set: *environmental* (covering aspects relating to impact on local environmental quality; change in usage of natural resources; and impacts on biodiversity and ecosystems); *economic* (covering aspects relating to economic impact and appropriate technology transfer); and *social* (covering aspects related to alignment with national, provincial and local development priorities; and social equity and poverty alleviation). In addition, there is a general criterion that looks at whether the distribution of CDM project benefits are reasonable and fair.
Small scale projects	Defines thresholds for renewable energy CDM projects with a maximum output capacity equivalent of up to 15 MW; energy efficiency improvement projects which reduce energy consumption on supply and/ or demand side by up to the equivalent of 15 gigawattshours per year; and other projects that both reduce anthropogenic emissions by sources and that directly emit less than 15 kilotones of carbon dioxide equivalent annually.	Not defined.

5 CDM projects implemented: situation on the ground

As of July 2006, Morocco had 60 CDM project proposal at various stages of approval Ministry of Land-use Management, Water and Environment [8] whilst South Africa had a third of this at 20 Department of Minerals and Energy [9]. Of the 60 CDM projects for Morocco, three were registered with three others undergoing validation. South Africa on the other hand had two projects registered, none under validation and four with their PDDs approved by the DNA. Current Morocco's CDM projects have a potential of reducing 7 million tonnes of CO_2e annually and South Africa's can reduce about 9.5 million tonnes. Details regarding CDM projects status for both countries as of July 2006 are presented in figure 1.

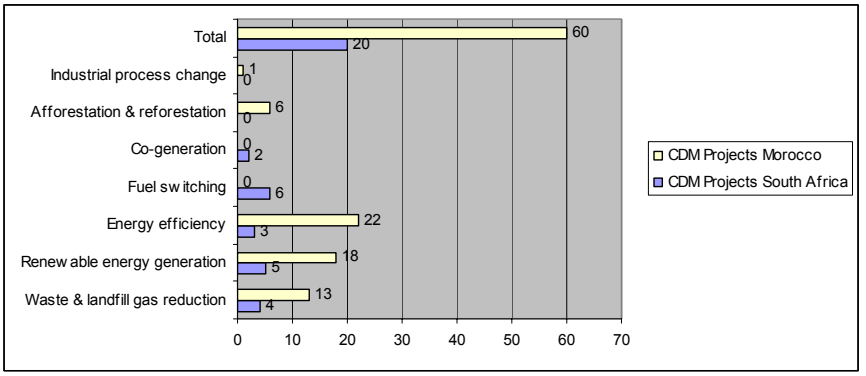

Figure 1: CDM project status as of July 2006 (n = 60 for Morocco; n = 20 for South Africa).

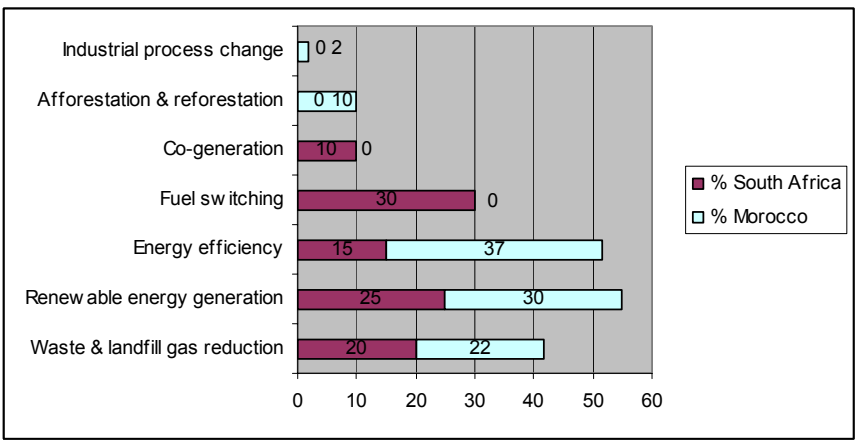

Figure 2: Sectoral distribution of CDM projects (n = 60 for Morocco; n = 20 for South Africa).

There are contrasting insights in terms of sectoral percentage distribution of CDM projects in the two countries (figure 2). Energy efficiency account for 37% in Morocco compared to South Africa's 15%. Similarly, there are no fuel switching and cogeneration CDM projects proposed for Morocco and these comprise 40% of South Africa's projects. Likewise, there are no industrial process change, afforestation and reforestation CDM projects in South Africa, whilst these constitute 12% for those in Morocco. Both the renewable energy; as well as waste and landfill gas CDM projects have fairly equal proportions in both countries. South Africa's DNA has recently prescribed thresholds for afforestation and reforestation CDM projects Department of Minerals and Energy [10]. The minimum values for forest thresholds are stipulated as: (a) a single minimum tree crown cover value of 30%, (b) a single minimum land area value of 0.05 hectares, and (c) a single minimum tree height value of two metres.

A summary of approved CDM projects, those under validation, those with approved PDDs as well as their capacity in terms of CERs for both countries is presented in table 4. In addition to CDM projects with status indicated above, there are 18 others whose PINs have been approved in Morocco and 13 in South Africa.

Table 4: Summary of approved CDM projects.

CDM Project Status	Morocco		South Africa	
	Project	CO_2e (tonnes)	Project	**CO_2e (tonnes)**
Registered	60 MW wind farm (Essaouira)	150,000	Kuyasa Low-Cost Urban Housing Energy Upgrade Project	**44,000**
	Photovoltaic kits to light up rural households in Morocco	39,500	Lawley Fuel Switch Project	**21,683**
	10 MW wind farm (Tetouan)	28,600		
Under Validation	Introduction of Heat Recovery System at Jorf Lasfar's chemical plant	84,800	None	-
	Biogas recovery and flaring (Oulija landfill)	13,800		
	10 MW Wind farm for the Tan Tan desalination plant	17,200		
PDD approved by DNA	Biogas recovery and flaring (Rabat Akreuch landfill)	76,00	Rosslyn Brewery Fuel Switching Project	**107,403**
			Bethlehem Hydroelectricity Project	**25,737**
			PetroSA Biogas to Energy	**30,000**
			Emfuleni Power Project	**763,960**
	Total (CO_2e)	409,900	Total (CO_2e)	992,783

6 Conclusion

This paper critically reviewed the CDM approval and evaluation criteria for Morocco and South Africa. The aim was to establish possible future competition points in attracting CDM foreign direct investment in these and other developing nations. The paper revealed significant differences in approval time frames and sustainable development criteria. It emerged that it takes about 42 days in Morocco for proponents to get responses on their proposed CDM projects compared to 60 days (if initial voluntary screening is excluded) and 90 days (if initial voluntary screening is included) in South Africa. The sustainable development criteria too, appear to be much stringent for South Africa compared to that of Morocco. By the time of writing this paper, 60 CDM project proposals had been submitted and were at various approval stages in Morocco compared to 20 in South Africa. Although the number of CDM project proposals submitted to the South African DNA is only a third of those for Morocco, their annual potential to reduce GHGs is much bigger. This stands at about 992,783 of CO_2e for South Africa compared to about 409,900 of CO_2e for Morocco. These figures show that effectively South Africa's realised potential is twice as much compared to that of Morocco. There is also a great chance that more CDM projects will be attracted into the forest establishments following the determination of the forest threshold by the DNA.

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First investigations on gas-phase mercury in two Italian cities

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Abstract

Mercury is an element naturally present in the biosphere of both natural and anthropogenic origins. From the chemical point of view mercury is present in the atmosphere in gaseous form as elementary mercury and Reactive Gaseous Mercury and adsorbed onto particulate matter over that in other forms in ultra-trace. From the toxicological point of view mercury is extremely toxic, reaches all the organs and it is also quickly absorbed by the lungs. In this study seasonal study campaigns were performed during 2005-2006 in two urban areas of different Italian cities, Taranto and Venice, to investigate the levels and behavior of gaseous-phase mercury. For the sampling and analysis a portable instrument was used based on the atomic absorption methodology with the background correction through the Zeeman effect. No relevant situations for human health were found (the levels range between 1 and 15 ng/m^3).
Keywords: mercury, urban pollution, human health, meteorological stability.

1 Introduction

Mercury is an element naturally present in biosphere: it can be of both natural (e.g. volcanic eruption, etc.) and anthropogenic (e.g. pig iron production, power plants or heat production, sanitary waste incinerators, etc.) origins. It is redistributed in atmosphere, in water and in soil doing so a very complex cycle of which only some passages are known while many other attend to be clarified. The interest for a greater knowledge of the mercury cycle in biosphere is

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connected to its level: in fact, because it represents a real hazard for human health it should be necessary to keep low its levels.

From the chemical point of view mercury is present in atmosphere in gaseous forms as elementary mercury (Hg^0) and Reactive Gaseous Mercury, RGM (e.g. $HgCl_2$), and adsorbed onto particulate matter (Total Particulate Mercury, TPM) over that in other forms in ultra-trace (e.g. methylated form) [1]. From the toxicological point of view mercury is extremely toxic. Elemental mercury vapor is highly toxic and is very hazardous to human health [2-4]. Mercury reaches all the organs (particularly, the kidneys) and besides it is quickly absorbed by the lungs [5]. As reported from other authors, the exposition risk is not only for people professionally exposed but also for people who reside or work in contaminated areas and individuals with amalgam fillings [6, 7].

Table 1 shows the levels of the different species of mercury reported in literature.

Table 1: Levels of the different species of mercury from literature. a: expressed as pg/m^3.

Species	Air (ng/m^3)	Wet dry (ng/L)
Total Hg	1.2-3.7	5-80
Hg^0	1.0-3.6	<0.005
RGM	1-50[a]	5-50
TPM	1-50[a]	5-50
Methylmercury	1-20[a]	0.005-0.5

Finally, a greater knowledge of the mercury cycle in biosphere is connected to the necessity to maintain low its level since it represents a real danger for human health according to two historical studies (Minamata, Japan, from 1953 to 1960 and Iraq population in 1971) allowing data acquisition of great importance on the toxicity from mercury, and then from other numerous following [8, 9].
For this reasons the World Health Organization (WHO) has more times affirmed the necessity to keep a high level of attention to the mercury exposure recommending also monitoring such pollutant [2, 3].

In this paper some study campaigns have been performed during the period April-October 2006 in downtown of two Italian cities, Mestre (a few kms away from Venice) and Taranto, in order to investigate the levels and the behavior of the total gaseous-phase mercury (Hg^0 and Reactive Gaseous Mercury).

2 Experimental part

2.1 Sampling sites

The two cities, Mestre and Taranto (Figure 1), have been chosen on the basis of their different urbanization: presence of industrial ports, different anthropogenic activities of great relief, urban installations not situated close to natural mercury

sources. In particular, Mestre is located in the North Italy whereas Taranto in the South Italy and in a region where, except Taranto itself, there are no strong anthropogenic activities.

The contexts studied can be considered as example of specific anthropogenic pollution, allowing so to collect data that can contribute to a best knowledge of the mercury presence in biosphere.

Figure 1: Map of Italy where Venice and Taranto are evidenced (Mestre is a few kms away from Venice).

2.2 Instrumental equipment

An RA-915+ atomic mercury spectrometer with an RP-91 attachment unit (Lumex, St. Petersburg, Russia) has been used as a mercury detector. A deep description of this instrument is reported by Pogarev *et al.* [4]. Here, we would like to briefly resume it. The RA-915+ is used for continuous mercury determination in air and for rapid analysis of solid and liquid samples. The spectrometer was placed in downtown of each city to investigate the mercury level and its behavior. Air flows continuously through the analytical cell. The blank signal is regularly checked by passing the air through a special filter with the Hg-absorption efficiency of 98-99%. The mercury concentration is measured every 15 s and processed.

The combination of the Zeeman Atomic Absorption Spectrometry using High Frequency Modulate light polarization (ZAAS-HFM) [10] and a multipath cell allows direct selective measuring of mercury at the background level up to 1 ng/m^3 with a response time of 1 s. The low detection limit (LOD) provides detection of remote or buried sources and high selectivity enables tracing mercury haloes in the presence of complex volatile compounds in air [11].

3 Results and discussion

From an analytical point of view it is interesting to investigate the possibility of this instrument that allows one to analyze the mercury level every 15 s in air. The LOD for this equipment has been established at 1 ng/m^3, analyzing the standards and the comparison with other spectrometric techniques.

Typical daily Reactive Gaseous Mercury concentration trends in Mestre (North Italy) and Taranto (South Italy) are reported in Figures 2 and 3, respectively.

First of all, analyzing Figures 2 and 3, it can be possible to evidence quite similar average mercury levels in the two different zones investigated. In particular, extrapoling for the whole period, average levels of 2.36 ng/m^3 and 2.92 ng/m^3 for Venice e Taranto, respectively, are found.

Furthermore, from Figure 2 the daily RGM trend is almost the same and no typical behavior can be noted: the only interesting data is the peak on the early morning of October 12th when the mercury level reaches almost 11 ng/m^3. In particular, this level is reached for a while due maybe to a local emission. Figure 3 shows a situation little bit different where a regular trend during the days can be evidenced: the daily behavior is characterized by growing levels during the early morning with a relative maximum peaks during the midday and, after it, by decreasing levels down to the afternoon when the minimum relative quote is reached.

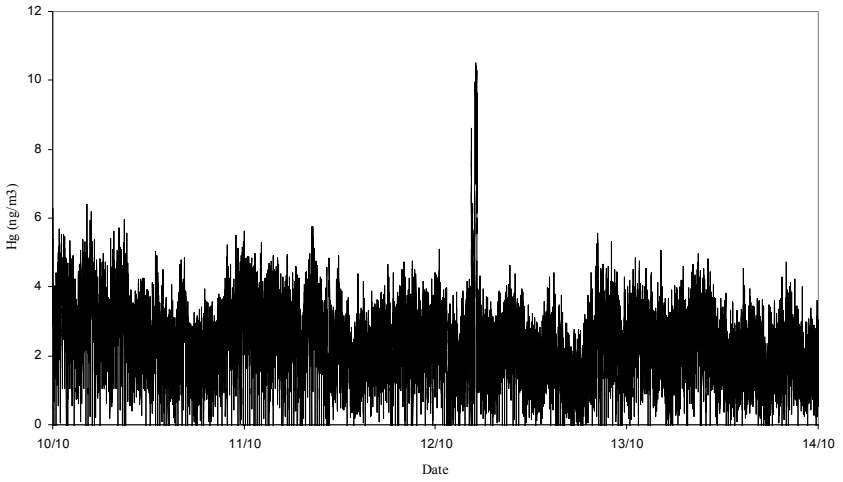

Figure 2: Daily RGM concentration trends in downtown Mestre (October 2006).

Furthermore, the maximum peaks recorded every midday demonstrate regular emissions both from same source and same direction (W-SW). The identification of this source is not easy to individuate because it should be necessary to know

exactly the anthropogenic activities (and eventually the presence of particular natural sources) in that area but it should be considered that this emission is not so strong and consequently the maximum reached peak is 8 ng/m^3.

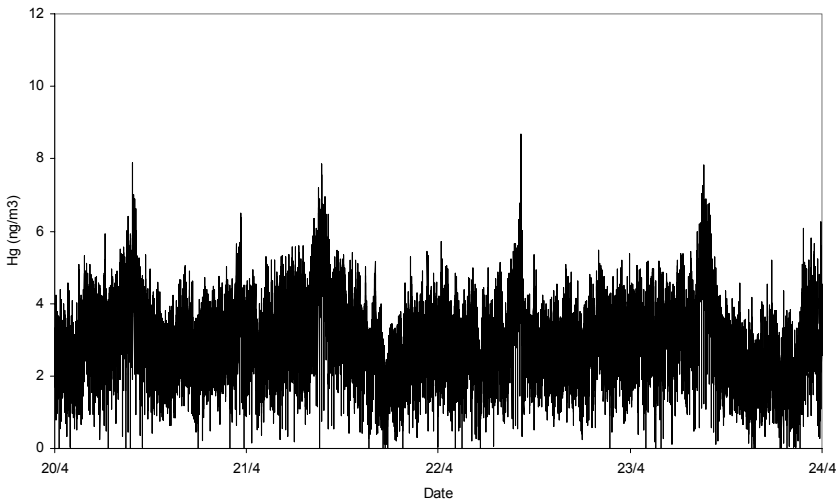

Figure 3: Daily RGM concentration trends in downtown Taranto (April 2006).

4 Conclusions

This paper reports the preliminary results of an investigation on the mercury levels and behavior carried out in two Italian cities. No relevant situations for human health were found (the levels range between 1 and 15 ng/m^3 according the areas). Finally, the mercury levels and behavior have been discussed to the atmospheric stability conditions. It should be noted that these data represent the first systematic investigation of this pollutant in Italian urban cities.

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Section 8
Indoor pollution

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Indoor air quality in Portugal: technical, institutional and policy challenges in the implementation of the directive on the energy performance of buildings (work in progress)

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Abstract

The implementation in 2006 of the Directive 2002/91/EC of the European Parliament and of the Council of 16 December 2002 on the energy performance of buildings in Portugal has brought new responsibilities to the Portuguese Institute for the Environment, namely the supervision of the Indoor Air Quality (IAQ) aspects in the Energy and IAQ National Certification in Buildings law. Following the transposition of the European Directive into Portuguese law, a Protocol was signed in July 2006, laying down the foundation for the establishment of qualified independent experts, in terms of minimum requirements and accreditation process.

Part of the role of the Institute for the Environment in this implementation process is to initiate, administer and participate in establishing an IAQ accreditation process to qualify a first tier of independent IAQ experts. These in turn will be responsible for future accreditation sessions. In preparation for this process, the Institute for the Environment has been initiating supervising and participating in the development of IAQ Certification and Management Plans, as well as in the IAQ accreditation courses that will take place in Portugal from October 2006 until April 2007.

This paper presents some aspects of the IAQ plans and procedures developed in Portugal for this effect. It sheds light on some of the technical, institutional, and policy challenges and highlights some of the constraints encountered so far. Special attention is given to the investment in the harmonization of existing IAQ knowledge, practices and procedures, and the effort needed to fill in some of the knowledge gaps observed.

Keywords: IAQ accreditation, IAQ Management Plans, IAQ Certification of Buildings, Portuguese IAQ policies.

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1 Introduction

The objective of this paper is to focus on the main technical, institutional and policy challenges in the implementation of the EPDB, rather than exploring the technical specifics of the IAQ policy. In fact, existing IAQ regulations in Portugal still lack technical amendments, as well as the rules that define the accreditation process of all specialists that will allow the full implementation of those regulations.

The implementation in 2006 of the Directive 2002/91/EC of the European Parliament and of the Council of 16 December 2002 on the Energy Performance of Buildings (EPBD) in Portugal has brought new responsibilities to the Portuguese Institute for the Environment. Although the EPBD focuses mainly on limiting outdoor carbon dioxide emissions through the promotion of energy efficiency, it also draws attention to the need to improve "indoor climatic conditions" in buildings.

It is the responsibility of the Institute for the Environment to supervise the implementation of the National System of Energy and Indoor Air Quality Certification of Buildings (Sistema Nacional de Certificação Energética e da Qualidade do Ar Interior em Edifícios, "SCE" in short), which transposes the EPBD in Portugal, in what concerns IAQ requirements in buildings.

In the national legislative context, the National System of Energy and Indoor Air Quality Certification of Buildings constitutes a tool to implement energy efficiency under the Energy National Strategy (Estratégia Nacional para a Energia) as well as under the National Program for Climate Change (PNAC – Programa Nacional para as Alterações Climáticas) in Portugal.

Following the transposition of the European Directive into Portuguese law, a series of national regulations (*Decreto-Lei)* were published in April 2006 [1–3] some of which repealed previous energy related regulations that were not always wholly implemented or fully adequate. Protocols were signed in 2006 between the various entities involved in the certification process to define procedures and minimum requirements for the accreditation of "qualified experts" (independent energy and IAQ experts) and heating ventilation and air conditioning (HVAC) installation, maintenance, and "IAQ-certified technicians".

Part of the role of the Institute for the Environment in this implementation process is to initiate, administer and participate in the accreditation of the first-tier qualified independent IAQ experts. These experts will in turn be responsible for future accreditation campaigns. In preparation for this process, the Institute for the Environment has been supervising and participating in the development of IAQ Certification and Management Plans, as well as in the SCE accreditation courses that is taking place in Portugal from October 2006 until April 2007.

2 IAQ regulations in Portugal

Prior to the introduction of the new indoor air quality requirements in the context of the energy and IAQ certification process, indoor air quality regulations in Portugal were limited to occupational health and safety guidelines.

These guidelines focused primarily on the quality of industrial microenvironments including their temperature, relative humidity, ventilation rates, and on toxic industrial chemicals such as benzene and formaldehyde.

In 2002, the Ministry of Environment drafted a legislative initiative that aimed the implementation of an indoor air quality law in non-industrial buildings, but it remained dormant. As a response to the increasing concern of exposure to air pollutants in indoor non-industrial environments this initiative was integrated in the existing air quality and energy efficiency regulations in the context of the transposition of the EPBD to Portuguese law in 2006. As a result, a comprehensive IAQ certification program will be implemented along with the energy efficiency certification of buildings in Portugal.

Table 1: IAQ Regulations.

Regulation	Contents / IAQ Requirements
Decreto-Lei 78/2006, April 4th National System of Energy and IAQ Certification in Buildings (SCE)	Sets the main rules of the certification national system. Refers to the need to maintain a good IAQ while pursuing energy efficiency goals.
Decreto-Lei 79/2006, April 4th Regulation of the Energy Heating and Cooling Systems in Buildings (RSECE)	Regulates the SCE in buildings with HVAC systems. Applies mostly to large new and existing service buildings. Includes IAQ requirements in terms of air renovation rates (new buildings) and maximum concentration of air pollutants (PM10, CO2, CO, O3, formaldehyde, TVOC), bacteria (including *Legionella*), fungus and radon (existing buildings). Also includes IAQ recommendations in the design and location of buildings.
Decreto-Lei 80/2006, April 4th Regulation of the Thermal Characteristics of Buildings (RCCTE)	Regulates the SCE in buildings without HVAC systems. Applies mostly to small new and existing service and residential buildings. IAQ requirements relate to temperature and humidity levels.
SCE Protocol, July 21, 2006	Sets the foundation for the creation of qualified independent experts, in terms of minimum requirements and accreditation process.
RSECE Protocol, November 2006	Sets the foundation for the creation of HVAC installation and maintenance, and IAQ certified technicians.

Table 1 lists the Portuguese regulations and protocols created so far under the EPBD, and summarizes some of the regulatory and procedure requirements as they pertain to indoor air quality.

3 IAQ audits, plans and procedures

IAQ audits will take place at three different stages during the construction and commissioning of buildings; (a) the building permit, (b) the use/occupancy permit, and (c) during the life of the building, as follows.

(a) Verification of IAQ requirements and issues in the project design: air change rates (taking into account air circulation patterns and ventilation efficiency), sources of pollution (materials, equipments and type of occupancy), and the location for air intakes.
(b) Verification of ventilation conditions, presence of unplanned pollution sources, and the presence of a comprehensive and adequate "IAQ Maintenance Plan".
(c) IAQ audit during the building's regular occupancy period, which includes the measurement of indoor air pollutants. The frequency of IAQ's audits during building's occupancy depends on the category of a building and its use.

An IAQ Maintenance Plan will be required for each building under the Regulation of the Energy Heating and Cooling Systems in Buildings, and will be prepared under the responsibility of the IAQ-certified technician. It will include information about the activities carried out in the building, equipments and materials used and the preventative maintenance procedures applied to guarantee a good indoor air quality, among others.

The qualified expert who conducts the audit will make the outcome of each IAQ audit available in an IAQ Report. If all IAQ requirements are met, the qualified expert, through ADENE, issues an IAQ Certificate. In case of non-conformity to IAQ requirements at the time of the audit, the qualified expert should include in the IAQ report relevant information and possible remediation actions that can be used in the development of the Corrective Measures Plan.

The owner of the building will be responsible for submitting the Corrective Measures Plan to the Institute for the Environment, pointing out improvements that will lead to compliance with good indoor air quality requirements. Following the implementation of the remediation actions mentioned in this plan, a follow up audit will be carried out to verify the conditions to either recommend further corrective measures or certify full IAQ compliance.

The IAQ certification in residential buildings to which the Regulation of the Energy Heating and Cooling Systems in Buildings applies is valid for ten years. Non-residential buildings such as office buildings will require IAQ certification every 2, 3 or 6 years, depending on their use.

All information pertaining to the National System of Energy and Indoor Air Quality Certification in Buildings process, including registration of Qualified

Experts and registration of energy and IAQ audits, IAQ Maintenance Plans, IAQ Corrective Measures Plans, will be centralized in a database at the Energy Agency (ADENE) in Lisbon.

4 IAQ in Portugal: challenges, constraints and opportunities

The main challenges associated with the consideration of IAQ requirements in the current law and, specifically, in the context of energy efficiency objectives, include technical, institutional and organizational issues.

The first step in the certification process consisted in the definition of the minimum qualifications required from and training needs of first-tier professionals that will become the national IAQ experts, the future and the main agents of the energy efficiency and IAQ certification process. The Institute for the Environment worked closely with existing IAQ professionals from national institutions and academia including IAQ researchers, microbiologists, and chemists and have consulted with members of relevant professional associations such as engineers and architects as well as related agencies to support the overall objectives of implementing an IAQ law in Portugal.

Air quality professionals have been working together with the support and supervision of the Institute for the Environment towards the development of IAQ procedures, management and plans including sampling methods and other aspects related to the IAQ certification process.

A considerable effort has been employed to link the different parties involved in the IAQ certification process. Each party brought its own view with different levels of expertise. Most of the parties involved have had an active role in the development of the National System of Energy and Indoor Air Quality Certification in Buildings with diverse responsibilities in the certification process. Table 2 lists the main parties involved in the process with respective roles.

Policy challenges related to IAQ are partly due to the lack of awareness by the public, and technical and policy agents, of the role of indoor air quality in public health and, consequently, in the human capital and its productivity. Given this challenge and the close and often conflicting energy efficiency and IAQ objectives, the Institute for the Environment has its own challenge. On the one hand, it needs to bring together the existing expertise in the areas of indoor air quality and public health and, on the other hand, it needs to integrate indoor air quality objectives and resources in the existing and partly implemented energy efficiency policies and resources so that both objectives can be simultaneously and seamlessly attained.

Another aspect worth mentioning is that contrary to what happens in regard to energy efficiency policies and related actions, indoor air quality issues have not been present in previous energy policies and regulations, nor has the Institute for the Environment had any previous regulatory responsibilities in indoor air quality. The past experiences of the Institute for the Environment in IAQ has been limited to air sampling and analysis provided by its laboratory in cases of indoor air quality investigations, as well as expert services in court cases.

Currently, most IAQ sampling and analysis in Portugal is being conducted by public laboratories, universities and some private sector companies.

Table 2: Main IAQ certification parties and their roles.

Entity	Role
Institute for the Environment (IA)	SCE-IAQ Supervision. Certification of Qualified Expert Instructors. Definition of minimum requirements for Qualified Experts. Accreditation of IAQ certified technicians.
Energy and Geology Directorate-General (DGGE)	SCE-Energy Supervision and Judicial enforcement (fines). Certification of Qualified Expert Instructor. Definition of minimum requirements for Qualified Experts.
Inspectorate-General for the Environment and Spatial Planning (IGAOT)	SCE - IAQ Judicial enforcement (fines)
Energy Agency (ADENE)	SCE Management and Inspection
Professional Engineers Association (OE), National Association of Technical Engineers (ANET), Professional Architects Association (OA)	Accreditation of candidates to Qualified Experts, curricula approval, etc. Definition of minimum requirements for Qualified Experts.
Public Works and Transportation High Council (CSOPT)	Definition of minimum requirements for Qualified Experts.
Professional Instruction Center for Thermal and Energy Industry (APIEF), HVAC Industry Portuguese Association (APIRAC), HVAC Engineers Portuguese Association (EFRIARC)	Accreditation of IAQ certified technicians.

Ongoing IAQ courses aiming the accreditation of lecturers who will start their own courses to certify the first-tier qualified IAQ experts required an intense harmonization effort. The Institute for the Environment coordinated harmonization workshops that brought together all those responsible for those courses, and that allowed an unprecedented exchange of technical and scientific materials as well as a constructive discussion over the interpretation of the law with respect to new procedures and methodologies.

IAQ courses have focused on various topics, including: the regulatory process and agents; indoor air pollution physical, chemical and microbiologic characterization; indoor air pollution sources and health effects; preventive and corrective IAQ measures with focus on the HVAC systems; IAQ sampling, measurement and analysis; IAQ audits, reporting and case study.

5 Work in progress

At the time of the writing of this draft paper (December 2006), the first Courses for Qualified Expert Lecturers (RSECE IAQ Module) have started, and it is expected that the IAQ Certification Module will take place in the first trimester of 2007. In addition to the role of the Institute for the Environment in coordination of the harmonization workshops for RSECE IAQ Module, and participation in the harmonization workshops for the IAQ Certification Module, technicians of the Institute are also providing lecturing services in both modules.

The Institute of the Environment is currently coordinating and supervising a team of IAQ professionals, in the preparation of Amendments (*Portarias*) to the national laws with respect to indoor air quality issues. These amendments will initially focus on the definition of sampling procedures, and the revision of the maximum allowed concentrations of indoor air pollutants, bacteria, and fungus.

The Institute of the Environment also provides technical support to the Energy Agency (ADENE) in all matters related to IAQ issues and procedures, and works alongside with IAQ professionals towards the full and up-to-date implementation of IAQ requirements in the national law.

6 Lessons learned

The work performed so far to attain IAQ requirements under the current certification regulations has been based on two main features: joint efforts and a multidisciplinary approach. The indoor air quality field is highly fragmented. It can only be put to practice if the various parties join their experiences towards a common goal. Likewise, IAQ polices have to be integrated into existing energy policies in order to minimize the gap between opposite goals in a cost-effective manner.

There is a need for a considerable increase in the exchange of expertise and information as they pertain to IAQ monitoring, auditing, and policy implementation procedures. This information exchange is needed to maximize the benefits of past, present and future efforts to protect public health in the environments where we spend most of our time, in home and at work.

It is also essential the safeguarding of a continuous effort that will integrate new findings about IAQ (sources of indoor pollution, materials with lower emissions, new ventilation & HVAC technologies, etc), better information to the public about the relationship between IAQ and public health, and procedures that guarantee the full achievement of IAQ policy objectives.

We can only hope that the transposition of the EPBD into national laws in Europe will contribute to that intention.

Acknowledgements

The authors would like to thank all those involved in the joint effort to implement IAQ requirements in Portugal, in the context of the transposition of

the EPBD. The authors are deeply thankful to Soheil Rastan and Pedro Restrepo for their contribution and encouragement.

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[3] Decreto Lei 80/2006 de 4 de Abril, Regulamento das Características de Comportamento Térmico dos Edifícios (RCCTE)

Identification and evaluation of the volatile organic compounds in working environment areas at a material recycling facility

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Abstract

Volatile organic compounds (VOCs) are major components of air pollution. It is well recognized that exposure to certain types of VOCs may cause occupational health effects such as respiratory disease, eye irritation, immune and neurological damage, and reproductive and endocrine disorders.

Different techniques are used to identify the VOC concentration that workers may be exposed to in the working environment. In this study, real-time monitoring of VOC was determined in August and September 2006 using a MiniRAE 2000 PID at a Material Recycling Facility (MRF) in Wales, UK. An inspection of the site was undertaken before the measurements were made to assist us determine the appropriate sampling locations, and to fully understand the operations at the MRF.

Benzene, Toluene, Ethyl benzene and Xylene (BTEX) were detected at different working environment areas at the MRF. Although the values monitored were low and are unlikely to have any primary health effects, it is worth investigating any unpleasant odours that may cause secondary symptoms
Key words: air pollution, material recycling, emissions, VOCs

1 Introduction

Although several researchers have addressed the risk of waste facilities, for instance congenital anomalies and malignancies in relation to living in close-proximity to landfill sites, the health impacts of new waste management technologies and the increasing use of recycling and composting is an area that always require further assessment and monitoring Rushton [1], Megrahi *et al.* [2].

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There are several initiatives in various parts of the world that encourages the public to recycle waste, which is usually taken to Material Recycling Facilities, MRF, to be sorted. The types of Material Recycling Facilities vary from MRFs that only bale source separated materials to Single Stream facilities that use appropriate sorting methods to prepare recovered materials for market.

No work that we have come across has been published on the levels of volatile organic compounds, VOCs, in a manual sorting MRF, and this paper provides data on levels determined at an MRF site in Wales, UK.

Although indoor VOCs have been found to cause asthma-like symptoms Norback *et al*. [3], there is little epidemiologic work on ambient exposures. There are no data on relationships between respiratory health and exhaled breath VOCs, which is a biomarker of VOC exposure. Pappas *et al*. [4] study concluded that reductions in levels of VOC to substantially less than 25 mg/m^3 are required if a "non-irritating" work environment is desired. In regions of high traffic density, stronger associations for ambient than for breath VOCs have been determined suggesting that ambient VOC measurements are better markers for daily exposure to combustion-related compounds thought to be causally related to acute asthma Delfino *et al*. [5]. There is now evidence that VOCs play a role in exacerbating respiratory symptoms Beck *et al*. [6].

2 Materials and methods

The MRF site chosen for this study is located in Wales, UK, and waste materials delivered at the site are sorted manually. In a week, the MRF site receives 160 tonnes of domestic municipal waste and 660 tonnes of commercial waste. The waste is separated manually on a segregation line and then baled.

Before the measurements were taken, a pre-inspection survey was completed and the information gathered used during the walk-through the facility to assist the authors to be familiar with the operations at the MRF.

Real-time monitoring of VOC was determined using a MiniRAE 2000 PID. Monitoring was determined on four periods during an 8-hour working shift - four in August and one in September 2006. The levels were monitored at the beginning, middle-point and the end of the sorting line.

The PID was selected because of the portability, size, ease of use and data logging capabilities. The PID was calibrated using isobutylene. Air was drawn through the PID at 450 ml/min. The PID was equipped with a 10.6 ev lamp and measurements taken every second. All data were stored in non-volatile memory, and later downloaded to a computer and analysed. The MiniRae PID provides the most cost-effective detailed exposure assessment for solvent mixtures Coy *et al.* [7], and it has been used to monitor organic compounds Walsh *et al.* [8], Simpson *et al.* [9], Preller *et al.* [10], Enomoto [11]. The response of the portable PID used to monitor VOC has been found to highly correlate to the standard charcoal sorbent tubes, analyzed by gas chromatography, results for hydrocarbon mixtures encountered during various painting tasks Coy *et al*. [7] The MiniRae PID is compliant with the specifications contained in EPA Method 21 (40FR) for leak detection and monitoring of fugitive emissions.

3 Results and discussion

The results from the survey identified the common VOCs to be Benzene, Toluene, Ethyl benzene and Xylene (BTEX), Table 1.

Table 1: Average BTEX levels in ppm on the sorting line at the MRF.

	Beginning	Middle	End
Benzene	0.29	0.40	0.21
Toluene	0.27	0.39	0.2
Ethyl benzene	0.28	0.39	0.20
Xylene	0.25	0.57	0.18

The levels of BTEX determined at the beginning of the segregation line in August and September 2006 are shown in Figures 1 and 2, while the variation of benzene at the end of the segregation line is shown in Figure 3. The contribution to the BTEX values at the 3 sampling points is shown in Figure 4.

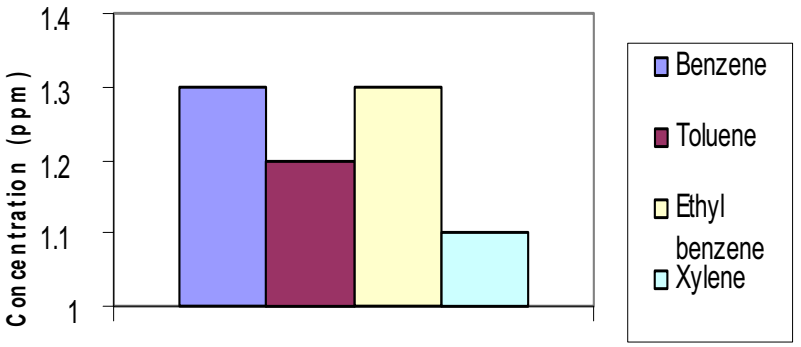

Figure 1: Average VOCs at the beginning of segregation area 4 August 2006.

The BTEX average values observed at the MRF are low. However measurements made during the first monitoring period on 4 August 2006, were 1.3, 1.2, 1.3 and 1.1 ppm for benzene, toluene, ethyl benzene and xylene respectively. The corresponding measurements during the other periods were notably lower as the MRF had reduced the delivery of organic waste. In addition, there were marked improvements in working conditions including increased ventilation and the regular cleaning of the sorting line and the surrounding areas. From the walk-about survey, we had pointed out these measures to the MRF operator, and were delighted that their implementation resulted in a huge

reduction in BTEX concentration. The other areas we suggested changes were on site operation, and in the welfare and further training of the employees.

The VOCs, at these low concentrations have not been reported to have any primary health effects, but it is worthy investigating any unpleasant odours that may cause secondary symptoms such as nausea and hypersensitivity reactions normally reported in other types of waste facilities Muller *et al.* [12] and Tolvanen *et al.* [13]

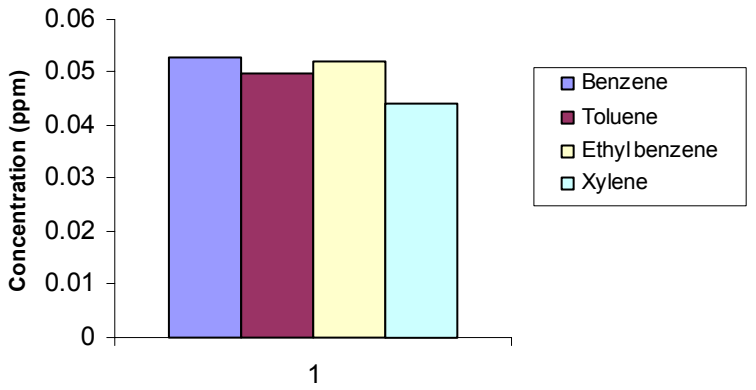

Figure 2: Average VOCs at the beginning of segregation area in September 2006.

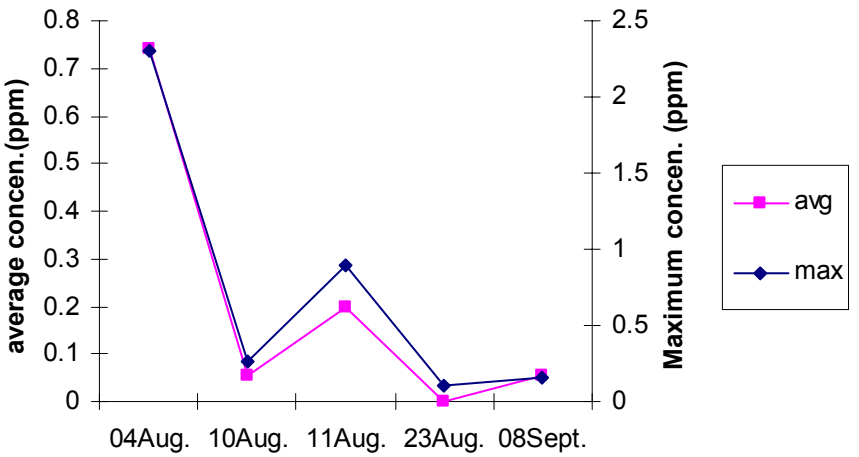

Figure 3: Variation of benzene at the end of segregation line.

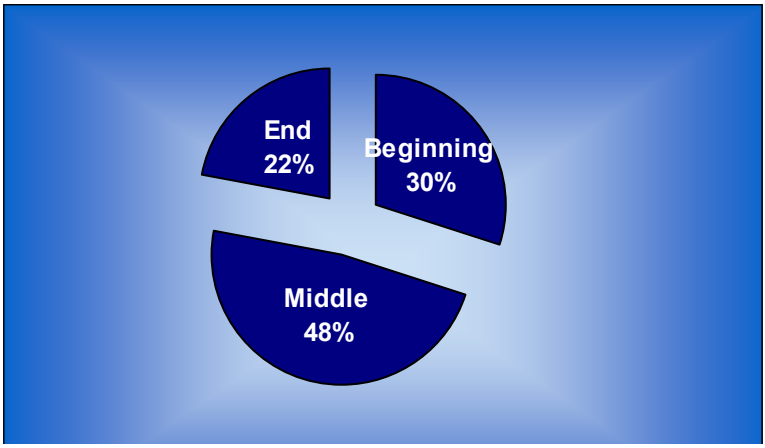

Figure 4: BTEX concentration in the 3 stages of the segregation line.

4 Conclusions

The data collected at the MRF shows that the PID is a useful tool for real time VOC measurement. Although the VOC concentrations were low, further improvement on the site that has taken place since September 2006 will continue to help improve the working environment at the site.
The paper has demonstrated how simple remedial measures in an MRF can reduce the pollutant levels that workers are exposed to.

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Gas phase photocatalytic oxidation of VOC using TiO_2-containing paint: influence of NO and relative humidity

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Abstract

Advanced oxidation process (AOP) such as photocatalysis is a promising technology for air purification. It is the purpose of this study to investigate the photocatalytic removal of volatile organic compound (VOC) using TiO_2-containing paints. The photocatalytic activity of the paint was studied in a walk-in type environmental chamber (30 m^3) under a realistic level of irradiation, humidity and VOC amount with reference to a typical urban air pollutant concentration. The effects of concurrent photodegradation of NO and VOC as well as the effect of the relative humidity level were also investigated in order to evaluate the feasibility of the photocatalytic building material (paint) for air purification under real conditions. It was found that the presence of NO promoted the photodegradation of toluene, under low humidity levels (17% RH), up to 15%. It was suggested that the enhancement of toluene conversion was due to the generation of $OH^{\cdot}$ radicals during the photodegradation of NO. Results were also showed that no photodegradation of toluene was found while increasing humidity up to 50%.
Keywords: photocatalysis, TiO_2, photocatalytic paint, VOCs, NO, air purification, relative humidity.

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1 Introduction

Conventional methods for treating VOCs from gas streams, such as absorption, adsorption, condensation and thermal/catalytic incineration have inherent limitations and none of them is cost effectively. Therefore there is a demand for a relatively cheap and environmentally benign process of removing organic compounds in low concentration from gases (Wang and Ray [1], Zhao and Yang [2]). Heterogeneous photocatalytic oxidation (PCO) is useful for the treatment of air polluted with volatile organic compounds (VOCs). It allows the oxidation of airborne VOCs into carbon dioxide and water at room temperature in the presence of a semiconductor catalyst (e.g. TiO_2) and UV light source (Maira et al [3], Blanco et al [4]).

Light excitation of TiO_2 seminoconductor, under a wavelength between 360-380 nm, generates electrons and holes in the conduction and valence bands, respectively. These species are very reactive and can either recombine or diffuse to seminoconductor surface where they are trapped by adsorbed molecules of water and oxygen. They provoke the formation of hydroxyl radicals that attack pollutant molecules and thus degrade them (Riegel and Bolton [5]). Accordingly, materials that use photocatalyst have a semi-permanent capacity for removing VOCs from the air. Therefore, if photocatalysts can be used in roadway structures, as outer material on buildings along roadways etc., the building materials will have the capacity to clean the air along the roadways that is polluted by automobile exhaust gases, using only the solar energy (Fujishima et al [6], Strini et al [7])

Although a wide range of common organic pollutants can be treated by PCO the effectiveness of the process for pollution abatement seems to depend on the chemical nature of the pollutant molecule. For example the photocatalysis rates for aromatic compounds are relatively slow comparing with the complete oxidation of alcohols or chlorinated hydrocarbons (Maira et al [3]). Among numerous compounds which belong to VOCs, toluene is chosen for this study. The reason is that toluene is the major VOC found in indoor as well as urban outdoor environment.

Previous photocatalysis studies have mainly focused on the photodegradation mechanism, catalyst deactivation and catalyst preparation (Demeestere et al [8], Hashimoto et al [9], Cao et al [10]). The concentrations of pollutants used in most of the studies were very high (thousands of ppbs), rarely found in normal and polluted urban environments (Devahasdim et al [11], Hashimoto et al [9]).

It is the purpose of this study to measure the photocatalytic activity of commercial paint towards toluene at realistic level of irradiation, humidity and pollutants concentration. The photocatalytic materials are used under real scale so it is important to photo-induce air pollutants under realistic environmental indoor (Maggos et al [12]) or/and outdoor (Maggos et al [13]) conditions. TiO_2-containing paint was spread over the surface of glass panels and placed into a stainless steel (30 m^{-3}) walk-in type environmental chamber in order to verify their effectiveness in removing toluene under controlled environmental conditions. The depollution activity of the material is presented as the percentage

of the pollutant eliminated during the photocatalytic process and as the mass of the pollutant destroyed per second per square meter of exposed active surface (photocatalytic rate). The velocity (cm s^{-1}) of the photo-induced removal/degradation of the pollutant is also calculated.

Previous studies have reported the significant impact of relative humidity and inorganic pollutants presence on the rate of VOCs photooxidation (Ao et al [14]). For that purpose, the photocatalytic degradation of toluene under different humidity levels and the effect of the presence of NO were investigated in this study.

2 Materials and methods

2.1 Experimental set up

Experiments were conducted in a 30 m^3 environmental chamber (Indoortron) made of stainless steel. Strict control of temperature, relative humidity as well as zero air quality was obtained in the chamber. The operating temperature was 23°C while the relative humidity (RH) was set to 20% or 50%. Three stainless steel fans ensured internal chamber air mixing. The U.V exposure unit consisted of four (4) U.V Osram Ultravitalux 300 W lamps fixed on a square support. The lamp set placed at 150 cm from the centre of the sample panel, in an upper position. The total U.V irradiance was 4.6 W/m^2 at the center and 2.1 W/m^2 at the corner of the sample panels (Maggos et al [15])

Controlled levels of polluted atmospheres were achieved by injecting directly in the chamber a known amount of concentrated pollutant. Toluene was injected in the chamber using a chromatographic grade compressed air stream (1 l/m for 10 minutes). VOC sampling was performed by means of tubes filled with carbopack and the analysis was performed using a GC-MSD (Gas chromatography – Mass Selective Detector) coupled with Automated Thermal Desorber (ATD).

2.2 Materials preparation

Two types of construction materials were tested. a) M1: mineral silicate paint treated with 10% TiO_2; and b) M2: water-based styrene acrylic paint treated with 10% TiO_2. Each sample set is composed of four 1 m^2 glass panels (total surface area 4 m^2).

The preparation of the test samples consisted of soaking, conditioning (drying) and activation with UV. At the end of the soaking process, aimed to remove salts from paints, panels were washed up with deionised water (Mill-Q grade) and placed in the Indoortron to be conditioned. The coated glass panels remained in the Indoortron at least 12 hours at 30 m^3/h air exchange rate, 23°C and 50% RH operating conditions for conditioning. After conditioning, samples were UV-activated for 8 hours using the experimental UV lamps unit described below. At the end of the activation process another conditioning cycle for at least 12 hours at 30 m^3 h^{-1}, 23°C and 50% RH conditions were performed. In order to

estimate VOCs emissions from the materials, air samples were taken during ventilation mode as well as after 7 hours in static mode. By the end of the preparation steps, samples were ready to be tested for their photocatalytic efficiency.

2.3 Catalytic activity calculations

The principle for the photocatalytic activity measurement is based on VOC loss. The VOC was introduced into the environmental chamber allowing toluene concentration of about 100 μg m^{-3}.

Inside the chamber, the incoming pollutant was consumed by four (4) mechanisms:

1. sink effect (on the walls of chamber);
2. absorption on the surface of the sample;
3. photolysis by U.V light;
4. photocatalysis by TiO_2 and U.V light.

Therefore, the measurement can give information on the TiO_2-material activity provided that the above side effects (1-3) have been taken into account. So, before performing the photocatalytic experiments, blank tests (material without TiO_2) were carried out in order to estimate the loss of VOCs due to side effects.

The following equations were used in order to estimate the catalytic activity of the materials.

(1) The percentage of VOC which were photo-removed was calculated by the following equation:

$$\%\mathrm{VOC}_{\text{photo-removed}} = \left(\frac{[\mathrm{VOC}]_{\mathrm{U.V}} - [\mathrm{VOC}]\mathrm{blank}}{[\mathrm{VOC}]_{\mathrm{U.V}}} * 100 \right)$$

where:

$[VOC]_{U.V}$ = The amount of VOC removed/degraded during the irradiation of TiO_2 containing sample (μg m^{-3})

$[VOC]_{blank}$ = The amount of VOC removed during the blank experiment (due to side effects) (μg m^{-3})

(2) The photocatalytic/oxidation rate (PR, μg m^{-2} s^{-1}) is calculated taking the sample surface, the chamber volume and the duration of the experiment into account. Thus, it provides a more precise estimation of the depollution capacity of a material than the percentage of photo-removal.

However, as PR is dependent on the concentration of the pollutant and as this concentration decreases with time, PR also decreases with time. Consequently, PR is in practice always calculated on basis of the first hour measurement.

$$\mathrm{Photooxidation-rate(PR)} = \left(\frac{V * [\mathrm{VOC}]_{\mathrm{TiO_2UV}}}{\mathrm{A} * \mathrm{t}} \right)$$

where:

$[VOC]_{TiO2\ U.V}$ = The amount of VOC removed photocatalytically from the system due to TiO_2 effect (μg m^{-3})

V = the volume of the experimental chamber (m^3)

A = Sample surface (m^2)

T = Irradiation time (s)

(3) The deposition velocity was also calculated in order to describe the photocatalytic activity independently of the pollutant concentration.

$$\text{Photocatalytic-}Velocity(PV) = \left(\frac{PR}{\frac{[VOC]_{in} + [VOC]_{uv}}{2}} \right)$$

where:

PR: The photocatalytic rate (μg m^{-2} s^{-1})

$[VOC]_{in}$ = The initial amount of VOC before turn on UV light (μg m^{-3})

$[VOC]_{uv}$ = The VOC concentration during irradiation phase (μg m^{-3}).

3 Results and discussion

3.1 VOC degradation activity

As shown in Table 1, styrene acrylic paint (M2) presents better photocatalytic properties than mineral silicate paint (M1). Approximately 8% of toluene is photocatalytically eliminated due to M1 TiO_2-containing paint while the corresponding value for M2 is more than 46%. Accordingly, the rate (μg m^{-2} s^{-1}) and velocity (cm s^{-1}) that toluene photo-induced were higher while using M2 paint.

Table 1: Toluene photocatalytic parameters.

Material	% Toluene Reduction	Photocatalytic rate (μg m^{-2} s^{-1})	Photocatalytic Velocity (cm s^{-1})
M1	8.46	0.011	0.008
M2	32.5	0.015	0.013

The results presented in Table 1 were obtained under experimental conditions of 23°C and 20% RH while no other compound was co-injected in the chamber than toluene.

3.2 Relative humidity effect

Figure 1 shows the impact of humidity on toluene photocatalytic elimination on both paints (M1, M2). The photocatlytic degradation of toluene decreases while increasing humidity from 20% to 50%. Actually, the photocatalytic activity was turned to zero regarding M1 paint while it was significant eliminated as far as M2 is concerned. In particular, the photocatalytic rate and velocity of toluene on M2 was reduced from 0.015 to 0.003 μg m^{-2} s^{-1} and from 0.013 to 0.003 cm s^{-1} respectively. This is probably due to the fact that as the humidity increases, more water vapor adsorbed on the TiO_2 surface, increasing competition for adsorption sites. It has been reported that humidity could have both positive and negative effects on the photooxidation rate of a pollutant (Einaga et al [16]). It is well known that water plays an important role in the photooxidation process since it contributes in the formation of active species (OH radicals etc.). However, the effect of humidity on the conversion of a pollutant also depends on its concentration (Ao et al [14]). At very low levels of pollutant (the case of this study) the competition for adsorption sites between toluene and water vapor is thousand times more than applying ppm level pollutants and only a small amount of water vapor is sufficient for the generation of OH radicals. Thus the photocatalytic activity decreases.

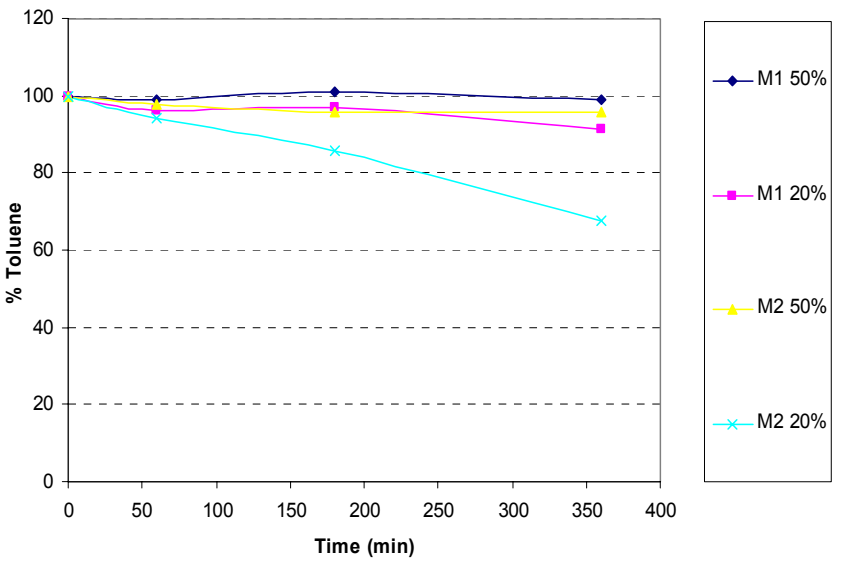

Figure 1: Photocatalytic degradation of toluene on M1 and M2 paints under different relative humidity levels.

3.3 Mixture effect

The effect of concurrent photodegradation of toluene and NO was investigated as both of them usually co-exist in indoor and urban environment. It was found that NO (~220 ppb) promoted the photodegradation of toluene on both samples under 23°C and 20% RH (Figure 2). NO presence increase toluene photodegradation from 8% to 14% on M1 while the increase for M2 was from 32% to 46.8%.

The enhancement of toluene conversion is due to the generation of hydroxyl radicals ($OH^{\cdot}$) during the photodegradation of NO as shown in eqs (1, 2):

$$NO + HO_2^{\cdot} \rightarrow NO_2 + OH^{\cdot} \quad (1)$$

$$NO_2 + NO + H_2O \rightarrow 2HONO \rightarrow 2OH^{\cdot} + 2NO \quad (2)$$

Thereafter, $OH^{\cdot}$ radicals react with toluene (adduction of OH radical to the aromatic ring) increasing the photocatalytic degradation of the pollutant (Ao et al [14]).

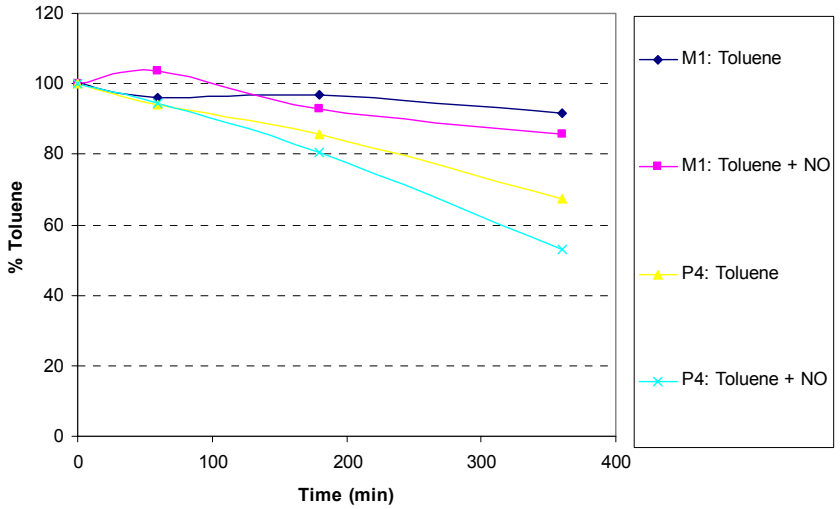

Figure 2: Photocatalytic degradation of toluene on M1 and M2 paints with and without the presence of NO (200ppb).

4 Conclusions

Two types of TiO_2-containing paints were tested for their ability to photo-induce VOC. The 8.46% and 32.5% of toluene were removed photocatalytically on M1 (mineral silicate paint) and M2 (styrene acrylic paint) samples respectively. Photocatalytic rate (μg m^{-2} s^{-1}) and velocity (cm s^{-1}) of toluene were also calculated for both samples. M2 sample presented better photocatalytic

properties than M1. The rate M1 degrades the organic pollutant was calculated up to 0.011 μg m^{-2} s^{-1} while the corresponding value for M2 were 0.015 μg $m^{-2}s^{-1}$. Humidity was found to significantly affect toluene photodegradation. An increase in humidity level from 20% to 50% inhibited the photooxidation of toluene on samples surface. In that case the photocatalytic rate decreased from 0.015 μg m^{-2} s^{-1} to 0.003 μg m^{-2} s^{-1} on M2 sample while the photo efficiency of M1 was totally eliminated.

On the other hand, the presence of NO enhanced the photodegradation of toluene on both samples. Co-injecting NO and toluene in the chamber increased the photocatalytic degradation of the organic pollutant on M1 and M2 sample from 8% to 14% and from 32% to 46.8% respectively. The formation of OH radicals, from the photocatalytic degradation of NO, consist the main parameter for the promotion effect of NO.

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