European status - Air quality: Trends, monitoring, background modelling

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1. INTRODUCTION

Over the last decades, aerosols have been subject of many studies which have considerably augmented the understanding of emission, atmospheric fate and deposition of aerosols (e.g. Lee et.al., 1985). The formation and growth of secondary aerosols from the oxidation of sulphur dioxide, nitrogen oxides, ammonium and VOC's, as a result of photo-chemical reactions in the atmosphere, is reasonably well understood and have been shown to be predominantly man made origin. The distribution of these secondary aerosols across Europe is also reasonably well known. Less information is available about the contribution of primary aerosols from anthropogenic and especially natural sources to the mass concentration of aerosols. Studies suggest, however, that their contribution may be significant (e.g. RIVM, 1996).

In most European countries, industrialization and high volumes of traffic mean that anthropogenic sources predominate, especially in urban areas. The most significant of these are traffic, power plants, combustion sources (industrial and residential) and agricultural activities. The main natural sources of airborne particulates in Europe are sea spray and soil resuspension by the wind. In addition, in the Mediterranean basin, Saharan dust and volcano emissions can also be important natural sources of particulates. Although the problems around particles has a long history, emission inventory activities are being undertaken only recently. (*Berdowski et. al., 1997a, 1997b).*

2. HISTORY AND TREND OF AIR POLLUTION BY PARTICULATE MATTER IN EUROPE

Particulate matter has, as already mentioned, a long history in Europe (Brimblecombe, 1987). One of the first quotations stems from the Roman philosopher Seneca who, already in 61 A.D., reported over the conditions in Rome as follows [Stern et. al., 1973]:

> "As soon as I had gotten out of the heavy air of Rome and from the stink of the smoky chimneys thereof, which, being stirred, poured forth whatever pestilential vapors and soot they had enclosed in them, I felt an alteration of my disposition."

Sterns continue to report that air pollution by particulates, caused by burning wood in Tutbury Castle in Nottingham, was considered 'unendurable' by Eleanor of Aquitaine, the wife of King Henry II of England and caused her to move in the year 1257. Somewhat later coal burning was prohibited in London. Looking to the more recent history can the period 1925-1950 be characterized as the period that present day air pollution problems and solutions merged. The Meuse Valley (Belgium) episode, one of the first occasions that excessive deaths were related to a period of elevated air pollution (smog), occurred in 1930. Although air pollution research got a start with first large-scale surveys (Leicester, England, 1939) no significant air pollution legislation or regulations were adopted. Only after the major air pollution disaster hit London in 1952 regulation started in Europe. Although the air quality in Europe has improved since then, the problem of particulates in the air has not been solved. In fact the second US-Dutch International Symposium in 1985 already about Aerosols (Lee et.al., 1986).

3. TRENDS

As a consequence of the long history of the problem many different measurement methods, describing different parts of the particulates in the air, exists now a day in Europe. New regulation (EU/DGXI, 1997) and harmonization activities (cf. CEN/TC 264/WG6) are momentarily in progress to improve this situation. See table 1 for the measurements methods in use (EU/DGXI, 1997) at national networks of EU countries.

Long term trends for PM_{10} are not available for Europe. Historically mostly TSP and black smoke has been measured. Long records are available for e.g. Paris, London, Birmingham, Manchester, Luxembourg, Brussels and Amsterdam (see figure 1). In all cases a strong downward trend in the 60's up to the beginning of the 80's can be observed. The reduced use of coal is the main reason for this downward trend. The increase of diesel traffic, especially visible in the black smoke measurements, flattens out the decrease since the late 80's.

In Europe, ambient concentrations of PM_{10} have been monitored in some urban networks since 1990, but there is currently no coherent overall European PM_{10} data set, mainly because PM_{10} has been systematically monitored only in a few member states (EU/DGXI, 1997). In addition, there is, momentarily no standardized method for monitoring PM_{10} across Europe, although standardization of PM_{10} measurement methods is under development (cf. CEN/TC 264/WG6) and expected to be adopted this year.

Previous studies and the data collected by the Working Group on fine particulates from EU-Member States (see table 2) indicates a reasonably consistent pattern of lower concentrations in the far north of Europe and higher concentrations, possibly due to naturally occurring particles, in the southern countries.

Measurements of $PM_{2.5}$ are still very scarce. Some primary measurements in the UK and The Netherlands suggest a ratio of $PM_{2.5}/PM_{10}$ of approx. 0.6. In the forthcoming particulate EU directive PM_{10} and $PM_{2.5}$ measurements will be mandatory in all EU member states.

An overview of the existing air quality networks and measurement data related to particulates can be found at the European Topic Center for Air Quality of the European Environmental Agency.

4. MODELLING OF FINE PARTICULATES

To describe the PM_{10} concentration a sub-division in 5 groups has been made:

- Primary emitted particulates (calculated by the EUTREND-model)
- Secondary inorganics (NO_3, SO_4, NH_4; calculated by the EUTREND-model)

- Secondary organics (no method available, rough calculates gives an average contribution of 1-2 ug/m^3 for Europe)
- Sea Salt (calculated, using scavenging ratio's, from rain water data)
- Soil resuspension (no calculation method available)

EUTREND

The long range transport model EUTREND is used for the calculation of the annual average mass concentrations of primary (PM_{10}, $PM_{2.5}$) and secondary aerosols (SO_4, NO_3, NH_4) over Europe on the basis of the earlier mentioned emissions inventory. The EUTREND model is an European version of the Operational Priority Substances (OPS) (van Jaarsveld, 1995). This family of models can be characterized as Lagrangian models in which the transport equations are solved analytically. Contributions of the various sources are calculated independent of each other using backward trajectories, local dispersion is introduced via a Gaussian plume formulation. Average concentrations are not determined from sequential (e.g. hourly) calculations but from concentrations calculated for a limited number of meteorological situations (classes) using a representative meteorology for each of the classes. Meteorological data is taken partly from the Numerical Weather Prediction model of the European Center for Medium Range Weather Forecasts (ECMWF) in Reading (UK) and partly from observations at meteorological stations all over Europe.

Dry deposition, wet deposition and chemical transformation are incorporated as first order processes and independent of concentrations of other species (Van Jaarsveld, 1995; Asman and Van Jaarsveld, 1992).

In the EUTREND model, five particle size classes are used, each characterized by a (monodisperse) particle size with corresponding properties calculated by the semi-empirical model of Sehmel and Hodgson (1980) which gives similar results as the more theoretical model of Slinn (1983). Concentrations and depositions are calculated for each of these classes and weighted with the percentage of the total particle mass appointed to the individual classes. Such an approach is especially useful for the modelling of primary-emitted particles because they usually cover a broad range of particle sizes, often including a significant fraction of large particles. Particle growth is

not incorporated in the present model but is implicitly assumed to take place in the lowest size-class (d < 1 (m). In support of the European Commission the EUTREND model has been used to calculated the primary and secondary contribution of these sources to the PM_{10} and $PM_{2.5}$ concentration in Europe.

Result of model calculations for rural background locations (using EMEP grids) for secondary inorganics and primary PM_{10} concentrations (using 1990 meteorology and emissions) are given in figure 2 and 3 respectively. For secondary aerosol an average contribution of 8.5 ug/m^3 (rural background between 0.6 and 24.9 ug/m^3) for the European Union has been calculated, with the highest background level in the eastern part of Germany (24.9 ug/m^3). For the primary emitted particulates an average contribution of 2.2 ug/m^3 has been calculated for PM_{10} (rural background between 0.2 and 15.9 ug/m^3) and 2 ug/m^3 for $PM_{2.5}$. The interpretation of these results should happen with some caution because the emission inventory used as input to the model is one of the first in its kind and needs still a lot of improvement and validation.

5. MODELLING OF SEA SALT

As part of its research on acidification RIVM has developed a method to determine the concentration of base-cations in ambient air from rain water measurements (Draaijers et al 1996). With some slight modifications this method has been applied to calculate the concentration of sea salt aerosols in ambient air.

Earlier studies have found (e.g.Woolf et al., 1987) that the typical diameter of sea salt aerosol, that is produced at the ocean surface by the bursting of air bubbles (a minimum wind speed of 3-4 m.s^{-1} is required), is 1-2 (m (although extending to sizes greater than 10(m). Therefore long-range transport of sea-salt aerosol can be expected. Using scavenging ratios, the air concentrations of these generated sea salt particles can be calculated from precipitation concentrations. Ambient air concentrations derived this way will reflect the large scale background situation.

The scavenging ratios were derived (Draaijers et al 1996) from simultaneous measurements of base-cations concentrations in precipitation and surface-level. This

approach is based on the premise that cloud droplets and precipitation efficiently scavenge particles resulting in a strong correlation between concentrations in precipitation and the surface-level air (Eder and Dennis, 1990). Scavenging ratios have been found reasonably consistent when averaged over one year or longer (Galloway et al, 1993). For this reason annual mean precipitation concentration has been used to infer annual mean air concentrations. The scavenging ratio (SR) is defined as:

$$SR= [C]_{rain}* \text{ Rho}/[C]_{air} \qquad [1]$$

Where $[C]_{rain}$ denotes the concentration in precipitation (mg/l, ~mg/kg), $[C]_{air}$ the concentration in ambient air (in ug/m^3) and Rho the density of air, taken as 1200 g/m^3. For the typical size range of sea salt particles the following relationship between the scavenging ratio and mass median diameter (MMD, in um) can be derived from data of Kane et al. (1994):

$$SR= 188 * e^{(0.227*MMD)} \qquad [2]$$

Rearranging equation [1] and [2] gives a simple empirical model describing the relationship between air concentration at one hand and precipitation concentration and MMD at the other hand (Draaijers et al 1996):

$$[C]_{air}= ([C]_{rain}*1200)/(188 * e^{(0.227*MMD)}) \qquad [3]$$

Precipitation concentrations will reflect atmospheric concentrations of the entire atmospheric column from cloud top to surface level and thus will reflect the large scale 'background' situation. A strong correlation with surface level air concentrations will only be present in well-mixed conditions at sufficient distance from sources. Close to sources surface level air concentrations usually will be considerably higher. As a consequence, near the coast the contribution of sea salt to the total suspended matter *in the surface level* air will be underestimated by using the method described above. On the other hand rain occurs mainly during western wind circulation's, leading to an *overestimation* of the yearly average concentration.

Composition of sea salt

Sea water contains sea salt to about 3.5% by weight, of which 85% is NaCl and it can safely be assumed that the sea-salt content of film and jet drops is similar. The composition of sea salt aerosols will change in relation to the distance to the coast due to the impact of continental air masses. For example, HNO_3 and H_2SO_4 present in continental air masses may volatilize Cl from sea salt and convert NaCl into $NaNO_3$ and Na_2SO_4, respectively, simultaneously releasing HCl(g) to the atmosphere (Mamane and Gottlieb, 1992). If Cl loss is suspected, one can compare the Na/Cl ratio, which is a good indicator of the Cl depletion, since Na is a conservative element. The Na/Cl ratio for the bulk deposition fluxes measured in The Netherlands is very close to the sea-water ratio (0.86), with a small gradient (0.86 to 0.91) over The Netherlands thus leading to the conclusion that Cl loss to the gas phase is insignificant for The Netherlands, See also Draaijers and Hulskotte (1997).

Based on the above described model and parameters the sea salt contribution, based on yearly averaged Na (sea salt $=3.25*[C]_{Na}$) concentrations in rainwater, has been calculated. The precipitation data were taken from Leeuwen et al. (1995). They compiled measurement results from approximately 600 sites scattered over Europe. To calculate the PM_{10} contribution, an average PM_{10}/TSP ratio of 0.7 has been used. The results are presented in figure 4. For the European Union countries the average, calculated, sea salt contribution to PM_{10} is 3.1 ug/m^3, with the highest contribution calculated for the west-coast of Ireland, 9.9 ug/m^3.

6. RESULTS FOR PM_{10}

In figure 5 the sum of the secondary inorganics, primary PM_{10} and the PM_{10} sea-salt contribution is presented. Comparing the levels presented in figure 5 with the measurements of PM_{10} levels in Europe, given in table 2, it can be concluded that there is still a large gap between predictions and measurements. This is especially large in South-Europe. The latter is probably due to natural sources as soil resuspension and Sahara sand who are not yet included in the model.

Also it is clear from the figure that the primary PM_{10} contribution is systematic smaller then the contribution from secondary aerosols. The average PM_{10} background concentration (defined as the sum of the calculated concentrations of primary PM_{10}, secondary inorganics and sea salt) in the Europe Union is, according to these calculation, 15 ug/m3, with a maximum in the eastern part of Germany of 42 ug/m3.

From the calcium concentration (aerosols) map (figure 6, calculated from rain water measurements, corrected for sea-salt contribution), that can be used as a rough indicator for the distribution of resuspended soil aerosols, a clear north-south gradient can be observed. Using the average abundance of Calcium in crustal material (2.1%) an average contribution of resuspended soil of 20 ug/m^3 can be calculated, with the highest contribution in Southern Europe (47 ug/m^3).

7. CONCLUSIONS

- Despite the enormous amount of research that has been carried out over the years our knowledge is still incomplete and more work has to be done, especially concerning the contribution of natural sources to PM_{10} and $PM_{2.5}$.
- Primary emitted particulate matter emission databases are now available, although improvement is needed.
- Primary results indicates that resuspended dust has an important contribution to PM_{10} concentrations in (South)-Europe.
- The contribution of secondary inorganics can be quantified adequately.
- The contribution of secondary organics can't be quantified yet, but results from US research projects indicates that the contribution will be probably small (1-2 ug/m^3)
- A first estimate of the contribution of sea-salt to PM_{10} aerosol in Europe has been presented.

REFERENCES

1. Annema, J.A., Booij, H., Hesse, J.M., Meulen, A. van der, Slooff, W, Integrated Criteria Document Fine Particulate Matter, National Institute of Public Health and the Environment, Bilthoven, The Netherlands, Report No. 601014015, 1996.
2. Asman, W.A.H. en Van Jaarsveld, J.A. (1992) A variable resolution transport model applied for NHx in Europe. *Atmospheric Environment* 26A, 445-464.
3. Berdowski, J.J.M., W. MulderIng C. Veldt, A.J.H. Visschedijk, P.Y.J. Zandveld. "Particulate matter emissions (PM_{10} - $PM_{2.5}$ - $PM_{0.1}$) in Europe in 1990 and 1993", Apeldoorn, The Netherlands, TNO/MEP R 96/472, 1997a
4. Berdowski, J.J.M. et. al., this proceeding, 1997b
5. Brimblecombe, P., The Big Smoke: A history of air pollution in London since medievaltimes, University Press, Manchester, 1987, ISBN 0-416-90080-1
6. Draaijers, G.P.J, Leeuwen, E.P, Jong, P.G.H. de, Erisman, J.W., Deposition of base-cations in Europe and its role in acid neutralization and forest nutrition, Bilthoven, RIVM, reportnr. 722108017, 1996
7. Draaijers, G.P.J. and Hulskotte, J.H.J. (1997), A literature study on some anthropogenic and natural sources of particulate matter in the atmosphere. TNO report no. R96/508.
8. Eder, B.K. and Dennis, R.L., On the use of scavenging ratios for the inference of surface-level concentrations and subsequent dry deposition of Ca^{+}, Mg^{2+}, Na^{+} and K^{+}, Water, Air and Soil Pollution, 52, 197-215.
9. EU/DGXI ,Ambient Air Pollution by Particulate Matter; position paper, concept report April 1997.
10. Galloway, J.N., Savoie, D.L., Keene, W.C., Prospero, J.M., The temporal and spatial variability of scavenging ratios for nss sulfate, nitrate, methanesulfonate and sodium in the atmosphere over the North Atlantic Ocean, Atm. Environ., 25A, 2665-2670
11. Kane, M.M., Rendell, A.R., Jickells, T.D. (1994), Atmospheric scavenging processes over the North Sea. *Atmospheric Environment*, 28, 2523-2530.
12. Lee, S.D., Schneider, T., Grant, L.D., Verkerk, P.J. (eds.) Aerosols, Research, Risk Assessment and Control Strategies, Proceedings Second U.S.-Dutch International Symposium on Aerosols, Wiliamsburg, 1985, ISBN 0-87371-051-7, 1986.
13. Leeuwen, E.P. van, Potma, C., Draaijers, G.P.J., Erisman, J.W., Pul, W.A.J. van

(1995), European wet deposition maps based on measurements. RIVM report no. 722108006, Bilthoven, The Netherlands

14. Mamame, Y. and Gottlieb, J. (1992), Nitrate formation on sea salt and mineral particles - a single particle approach. *Atmospheric Environment*, 26A, 1763-1778.
15. Sehmel G.A. and Hodgson W.H. (1980) A model for predicting dry deposition of particles and gases to environmental surfaces. *AIChE Symposium Series* 86, 218-230.
16. Slinn W.G.N (1983) Predictions for particle deposition to vegetative surfaces. *Atmospheric Environment* 16, 1785-1794.
17. Stern, A.C., Wohlers, H.C., Boubel, R.W., Lowry, W.P.; Fundamentals of air pollution, Academic Press, London, 1973.
18. Van Jaarsveld, J.A. van (1995), Modelling the long-term atmospheric behaviour of pollutants on various spatial scales. Ph.D. thesis, University of Utrecht, The Netherlands.
19. Woolf, D.K., Bowyer, P.A., and Monahan, E.C. (1987), Discriminating between the film drops and jet drops produced by a simulated whitecap. *Journal of Geophysical Research*, 92, 5142-5150.

Table 1. Particle Monitoring in the European Union (situation 94-96)

Type of monitoring	
PM_{10}:	9 countries[1]
Black Smoke:	9 countries
TSP:	8 countries
$PM_{2.5}$:	2 countries

[1] B-gauge (30 min-2h): 6 countries; TEOM (30 min-24 h): 6 countries;Gravimetry (24h): 2 countries

Source: EU/DGXI, 1997.

Table 2. PM_{10} measurements in Europe (1990-1994)

Country	Urban background		Urban Traffic		Urban Industrial	
	N	av. (ug/m3)	N	av. (ug/m3)	N	av. (ug/m3)
Sweden	5	12-16	1	35		
Finland	5	13-44[1]				
Denmark						
Ireland						
United Kingdom	13	20-34				
Netherlands	4	37-41	4	39-43		
Belgium						
Luxembourg	1	30	1	32		
Germany	2	36-65	1	50-58		
France	3	41-67	2	51-54	9	43- 78
Austria	1	40-42				
Portugal	1	72-75				
Spain	6	39-90			4	52-123
Italy						
Greece						

[1] One station 145 ug/m3

Source: EU/DGXI, 1997.

Figure 1. Trend particulate concentrations North-West Europe 1956-1996

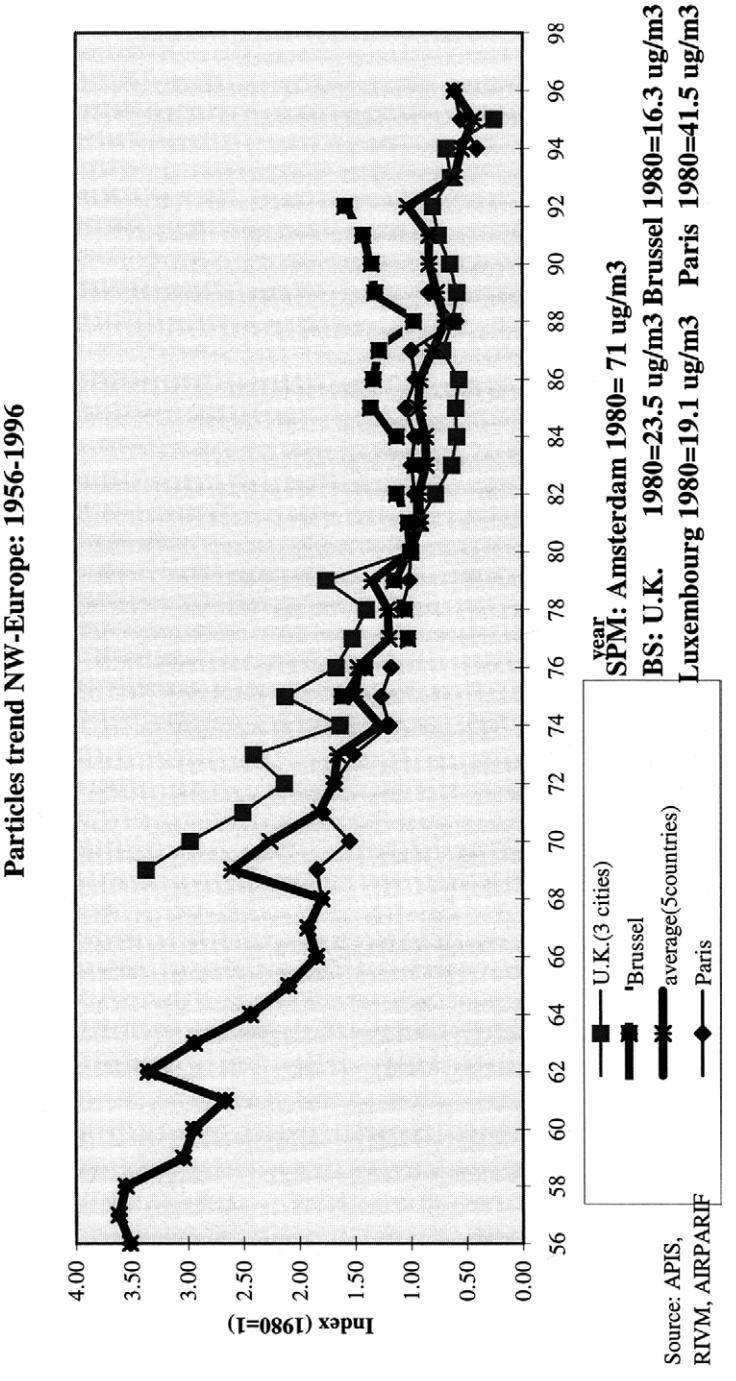

Figure 2. Primary PM_{10} contribution to PM_{10} concentrations of 1990

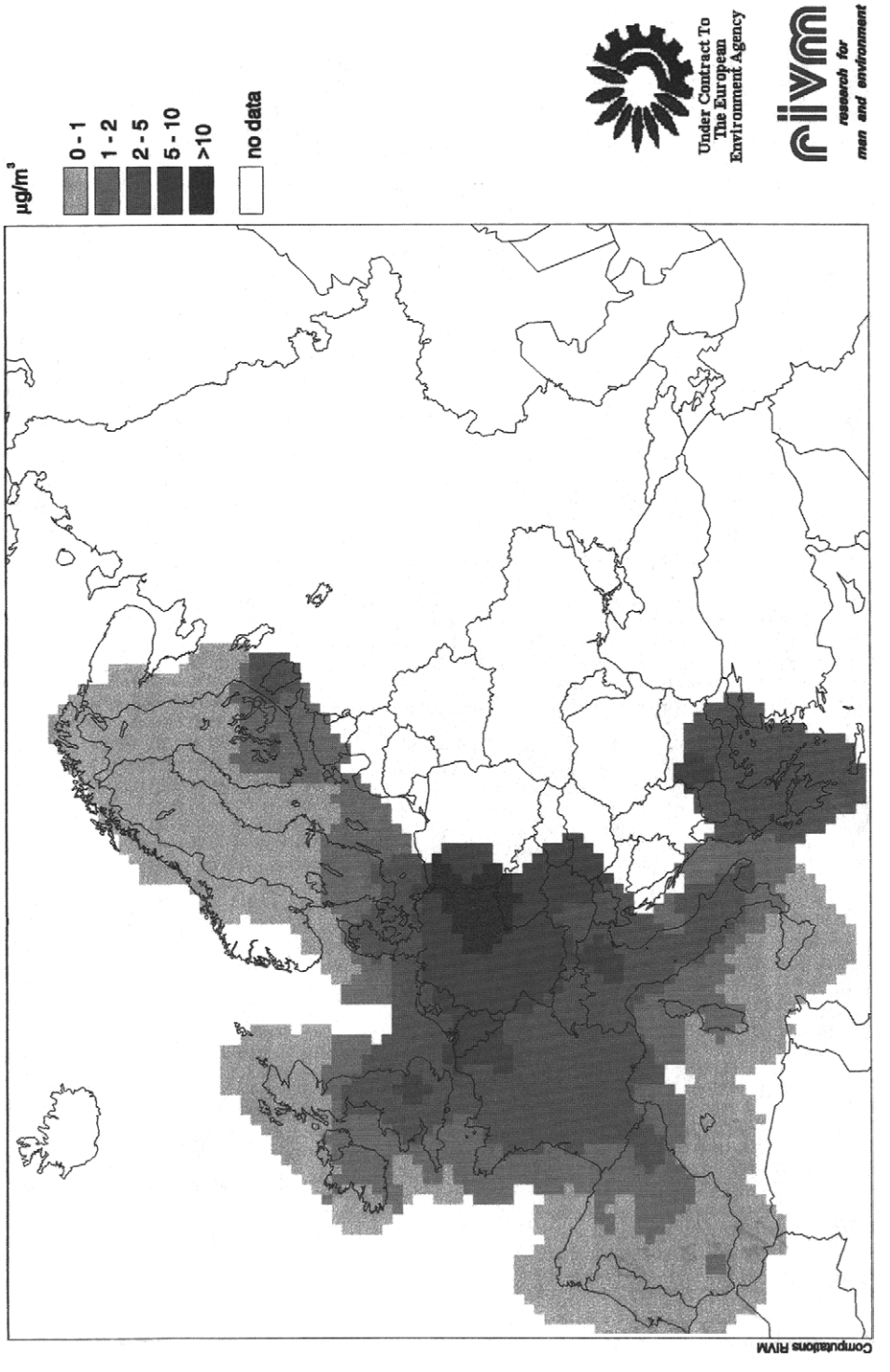

Figure 3. Contribution of secondary inorganics to the 1990 PM_{10} concentrations

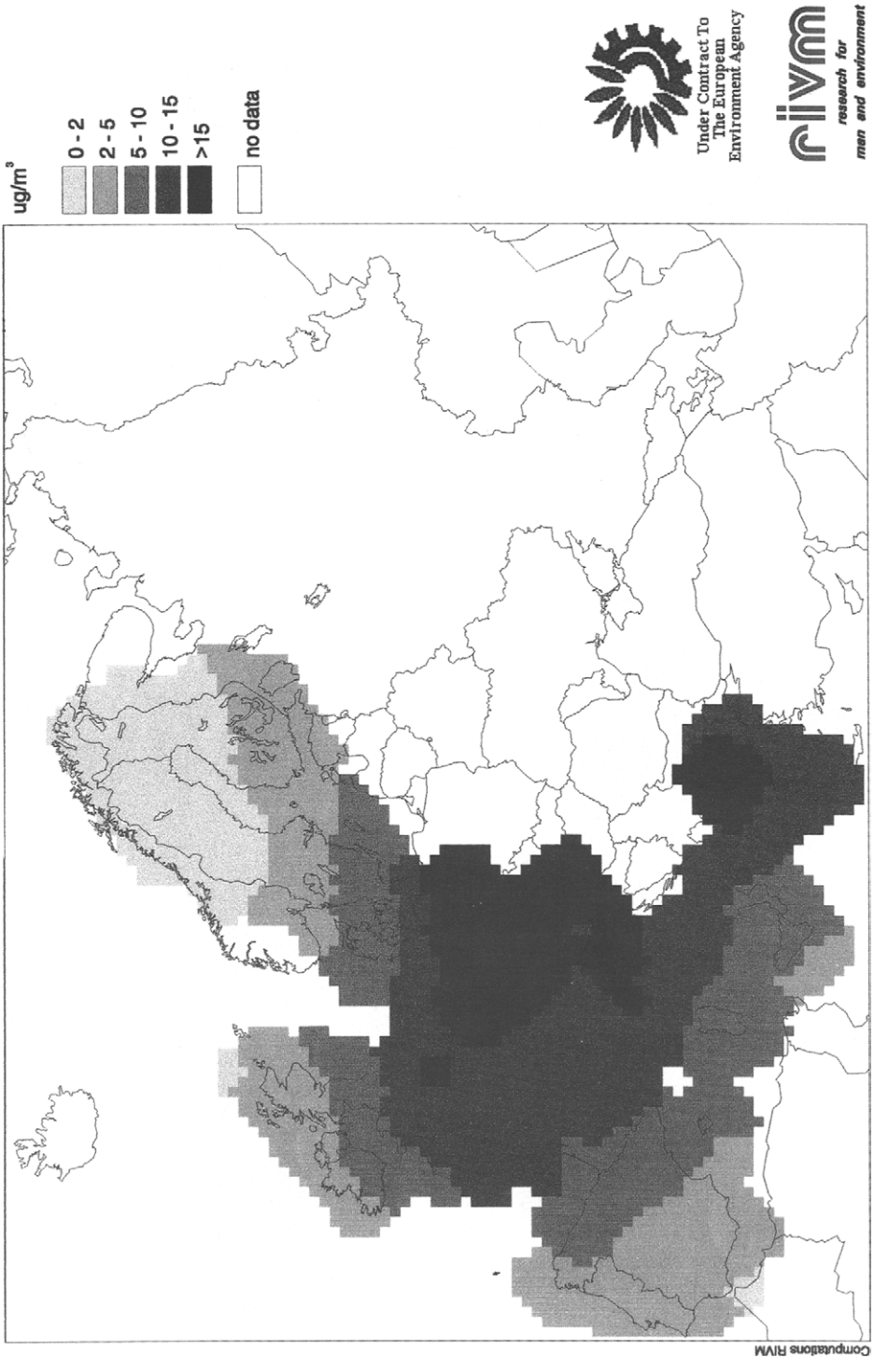

Figure 4. Contribution of sea salt particulates to the 1990 PM_{10} concentrations

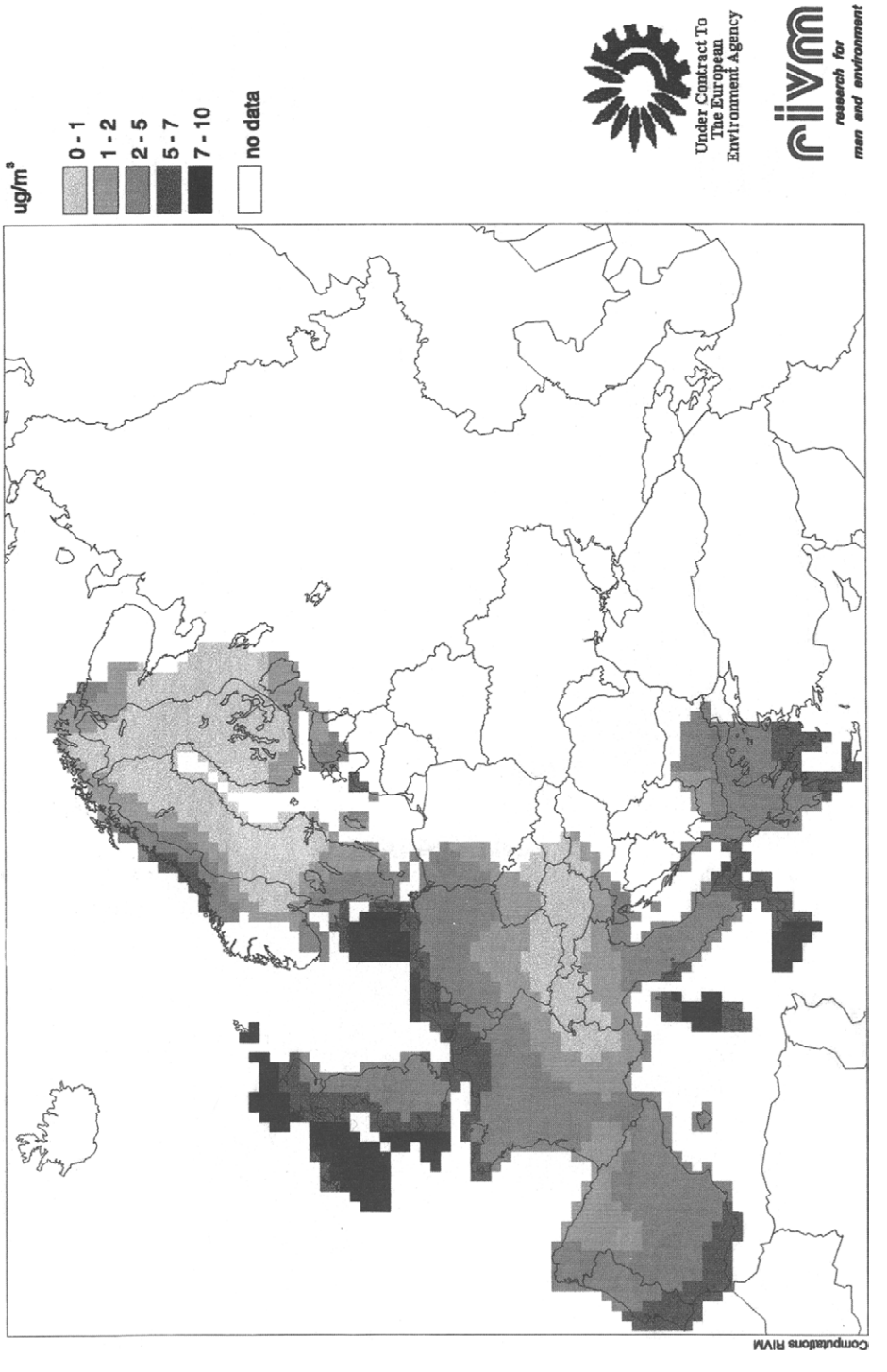

Figure 5. 1990 PM_{10} concentrations

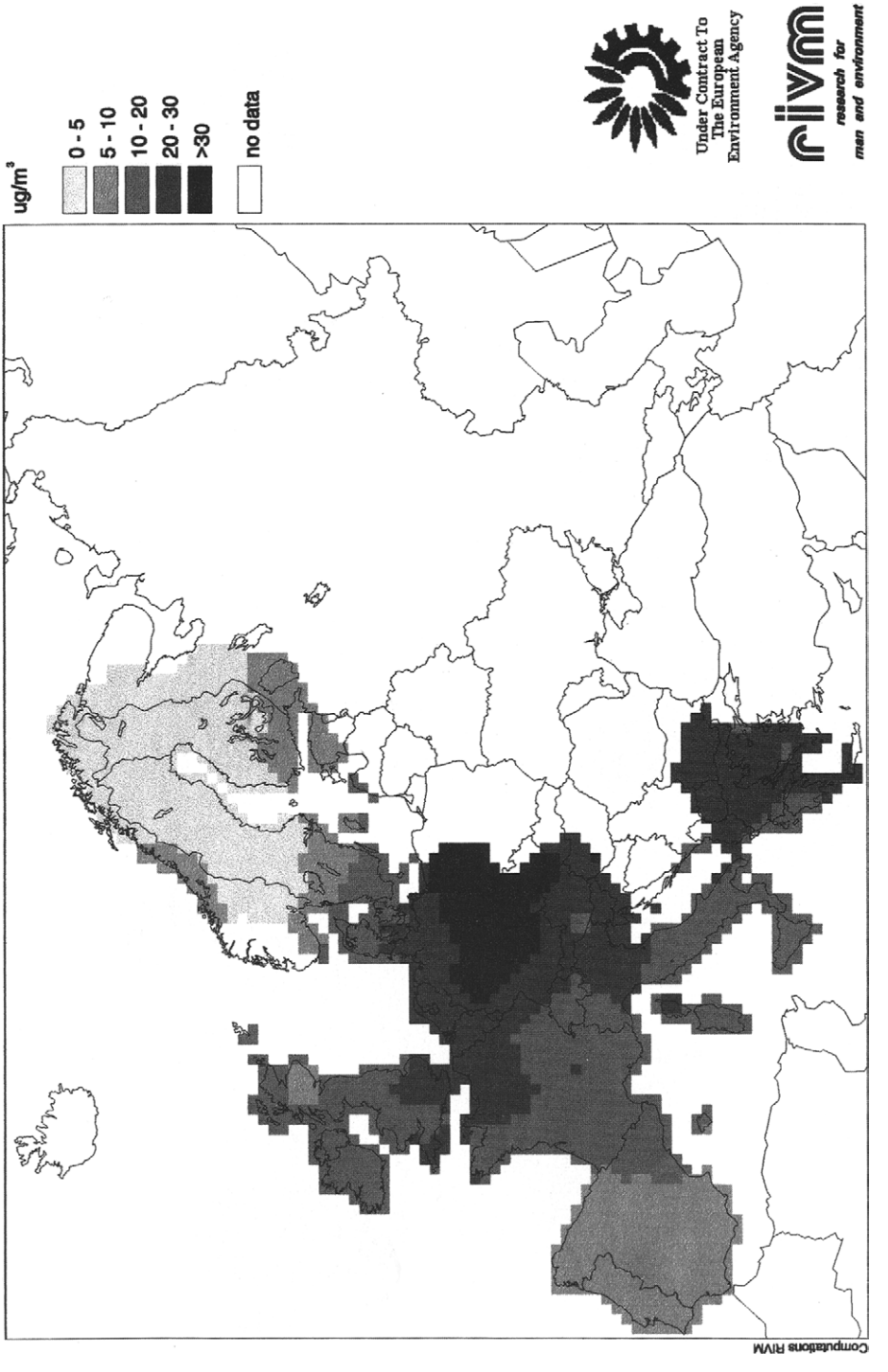

Figure 6. Calcium contribution (*47) to the 1990 PM_{10} concentration