Air Pollution Science for the 21st Century
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Chapter 10

New Directions: Fugitive emissions identified by chemical fingerprinting

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Air pollution monitoring techniques of increased resolution and specificity will become incorporated into pollution control strategies as they become available and economically viable. We speculate on how future technology may be used to identify fugitive emissions from industrial sources, which currently represent a deficiency in emission inventories and pollution legislation. Although we focus here on the situation in the United Kingdom (UK), similar arguments apply internationally.

In the UK an operator must gain Integrated Pollution Control (IPC) authorisation from the Environment Agency (EA) in order to operate a particular industrial process at a specific site. The focus of IPC in the UK has always been on emissions that result from the normal operation of industrial processes. Normal 'process' emissions are released from well-defined points on industrial sites such as stacks or vents and are relatively easy to monitor and quantify. In most cases authorisations cover explicitly only those emissions released in this way and take little account of non-process or 'fugitive' emissions. These unexpected or unplanned emissions are difficult to quantify in any meaningful way because they are released at non-specific points in space and time. They may result from ageing equipment, bad process management or the occurrence of accidents. In the case of industrial processes using, producing or involving volatile organic compounds (VOCs), fugitive emissions can account for a significant percentage of the total emission that will in reality be released from a site. That these emissions are not included in IPC authorisations for industrial processes is based more upon practicality than sound scientific rationale. The lack of authoritative information on the magnitude of fugitive emissions reflects both the difficulty and cost of monitoring at individual industrial sites, and the diversity of industrial processes that may produce them. Clearly, a technique that could be used to identify, quantify and attribute multiple fugitive emissions from a single monitoring point would be beneficial.

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The industrial component of emission inventories such as the National Atmospheric Emissions Inventory (NAEI) in the UK is compiled using data based directly upon the IPC authorisations issued by the EA. Clearly, there are major implications for operators, policymakers and scientists if a substantial component of industrial emissions is not properly quantified and included in emission inventories. A comparison of the total known emission of VOCs in the NAEI with monitored data shows the inventory to be underestimating emissions by around 40% (*Ozone in the United Kingdom: Fourth Rep. Photochemical Oxidants Rev. Group*, Institute of Terrestrial Ecology, Edinburgh, 1997). Significant progress towards validation of the inventory could be made by including industrial non-process and fugitive emissions.

Currently in the UK, 25 species of VOCs are monitored by the Automated Hydrocarbon Network across one rural and 11 urban sites. Gas chromatography (GC) methods provide high-resolution hourly VOC concentration data. Samples are analysed and the data automatically sent to the Department of the Environment, Transport and the Regions (DETR) database. Recent developments in the separation of VOCs suggest that in the future it will be possible to separate, identify and quantify a much greater number of compounds. A.C. Lewis, for example, has illustrated that whilst a portion of a conventional GC analysis of urban air revealed a dozen or so identifiable peaks, a two-dimensional "comprehensive" chromatography separation run in parallel revealed the presence of literally hundreds of different VOCs (New Directions: Novel separation techniques in VOC analysis pose new challenges to atmospheric chemistry, Atmospheric Environment, vol. 34 (2000) pp. 1155–1156). Once such techniques have been fully validated they will provide a far superior monitoring tool for the environmental manager.

The use of *chemical fingerprints* has been applied to the study of various atmospheric pollutants. Khallili et al. (Atmospheric Environment, vol. 29 (1995) pp. 533–542) used them to examine polycyclic aromatic hydrocarbons (PAHs) whilst Alcock et al. (Chemosphere, vol. 38 (1999) pp. 759–770) recently applied a fingerprinting technique to the identification of industrial sources of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated biphenyls (PCBs). A fingerprint can be obtained by monitoring and quantifying emissions from a particular industrial location. The emission of each compound will lead to an expected concentration in the air above the site. This air mass will have an identifiable composition of various VOCs at certain concentrations, representing the fingerprint of the source. As the air mass moves away from the site, it can be assumed that the initial changes in concentrations will relate to dispersion, and that this effect will be equal for all species. In the case of reactive species a model of atmospheric decomposition could be incorporated. Hence the concentration of components relative to one another can be predicted and the fingerprint will be identifiable at monitoring sites.

The focus of this article is to suggest how the use of industrial fingerprints combined with advanced analytical techniques could be used to identify fugitive emissions. The IPC legislation provides the regulating body (the EA in England and Wales) with emissions data for each industrial site. The formulation of a chemical fingerprint from each source is a straightforward process, requiring a dilution of the stack concentrations into the receiving air volume. We envisage that this approach will primarily be used in highly industrialised areas. Monitoring stations would be sited in locations where a number of point sources influence the air quality. At the monitoring station automated monitoring systems would be coupled to an atmospheric computer model. Inputs of source fingerprints and real-time meteorological data such as prevailing winds would assist in the identification of any sources influencing that area. Once key emission sources are located, we suggest that by matching the air quality data with chemical fingerprints, each fingerprint can be subtracted from the data to reveal any residual VOC emissions. It is these residuals that may indicate the presence of fugitive emissions. If a residual is always detected when a certain fingerprint dominates the atmospheric composition, it can be assumed with a reasonable degree of confidence to be linked to the fingerprint source. Hence this method can potentially be used to identify fugitive emissions from industrial locations. After a residual emission has been identified it should be possible to use a reverse-modelling approach to estimate the size of the emission at the source.

One problem may be the concurrence of other VOC emitters in the same area as the industrial sources of interest. In particular, vehicles are known to account for around 30% of the total VOC emission in the UK (*Fourth Rep. Photochemical Oxidants Rev. Group,* see above). Fortunately, in many cases the fingerprint of industrial sites may be of esoteric compounds that do not present in vehicle exhaust fumes. If this is not the case it should be possible to create fingerprints for petrol and diesel emissions and thus deduct their influence in the same way as for normal industrial process emissions. If necessary we envisage that this technique could be extended to other non-industrial VOC sources.

Identification of fugitive emissions would increase the accuracy of knowledge of both regulators and operators regarding the actual emission from industrial sites. The EA could assess the environmental impact of newly identified fugitive emissions in accordance with the current classifications of VOCs in terms of their harmfulness. If the chemical components of such emissions are relatively innocuous then the emission fingerprint may simply be added to the standard chemical fingerprint of the identified site. However, in the case of harmful compounds the regulator may require the improvement of environmental management systems. This may for example involve modifications to storage techniques, site operations and training of personnel. Economic benefits to the operators may become apparent with increasing efficiency in the use of raw materials.

A primary application of fingerprint identification of fugitive industrial emissions would be the validation and improvement of emission inventories, thereby reducing their tendency to underestimate concentrations of VOCs in comparison with monitoring data. As emission inventory data is improved in terms of speciation and accuracy of VOC emissions, identification of new compounds of interest in the atmosphere may also follow. It is likely that, as in the past, the focus of atmospheric chemistry will change as new species are highlighted due to their atmospheric concentrations or their effect upon human health or the environment.

Concepts such as photochemical ozone creation potential (POCP), global warming potential (GWP) and ozone depletion potential (ODP) are often calculated empirically using both monitored and emissions data coupled with a knowledge of atmospheric chemistry. For these concepts to be useful in a framework of international environmental policy making it is essential that the data upon which they are based is accurate and validated. If fugitive emissions are indeed as important as suggested here, then they play a significant and currently unquantified role in industrial air pollution. Improvements to POCP, GWP, ODP and emission inventories are likely to occur as a result of future implementation of the methodology proposed here. We therefore hope that the technology needed to monitor VOCs to the required specificity becomes available sooner rather than later.