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ENVIRONMENTAL CHEMISTRY GROUP

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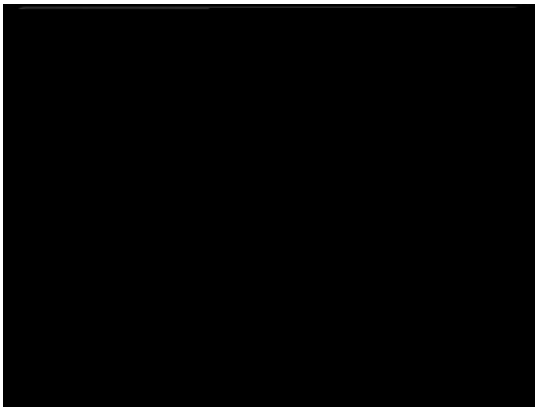
January 2007



CARBON DIOXIDE

1756: *Joseph Black reports his studies of carbon dioxide, or 'air fixed' in magnesium alba ($MgCO_3$) that is released by heating. He found that this fixed air was also generated when chalk ($CaCO_3$) is treated with acid. Black tested the gas and found that it extinguished rather than supported flames and discovered that when diffused into lime water (calcium hydroxide) the solution would turn cloudy. He also knew that it was denser than common air and demonstrated pouring the gas out of beakers onto flames to extinguish them. Black showed that the same 'fixed air' was produced by fermentation and respiration by demonstrating the clouding of lime water, a test still used in schools today.*

2006: *MEASUREMENT OF ATMOSPHERIC CARBON DIOXIDE: p. 2; ATMOSPHERIC CARBON DIOXIDE AS A CHEMICAL FEEDSTOCK: p. 18.*

The measurement of atmospheric carbon dioxide

There is a strong case for arguing that the accurate measurement of carbon dioxide in the atmosphere is the most important analytical challenge presented to contemporary chemistry. The initial uncertainties linking increased carbon dioxide levels to climate change voiced at the beginning of this century have been replaced by the economic and political realities of restricting our dependence on the combustion of fossil fuels, if we wish to avoid serious changes to the climate and to the environment. Key to the decisions that lie ahead in the next decade are the data on atmospheric carbon dioxide levels. **Paul Monks** from the University of Leicester, and an ECG committee member, describes his research group's collaboration in the measurement of atmospheric carbon dioxide using satellite-based analytical techniques.

ENVISAT

Retrieval of total columns of greenhouse gases with suitable accuracy and precision from space is a relatively new and challenging task. With the recent launch of the SCIAMACHY instrument on board the satellite ENVISAT (Figure 1), there is now an ability to measure the global total column amounts of a range of greenhouse gases (CO_2, CH_4 and N_2O) [Buchwitz *et al.*, 2000; Buchwitz *et al.*, 2004].

In the near future, NASA will launch the Orbiting Carbon Observatory (OCO) [Crisp *et al.*, 2004], the first dedicated space-based CO_2 mission, that is expected to sample the CO_2 columns with adequate precision and accuracy for carbon budget estimates to be made.

Figure 1: *ENVISAT is an advanced Earth observation satellite with a unique combination of sensors to vastly improve the range and accuracy of scientific measurements of the atmosphere, oceans, land surface and ice. Its total range of capabilities far exceeds those of any previous Earth observation satellite. It was launched in spring 2002 by an Ariane-5 launcher.*

Atmospheric carbon dioxide

Since the industrial era the atmospheric concentration of CO_2 has risen by ≈ 30% from 280 (±10 ppmv) to 367 ppmv in 2000 [IPCCC, 2001] with growth rates varying between 0.9 ppmv/yr and 2.8 ppmv/yr.

The increase of CO_2 in the atmosphere is caused by increased CO_2 emissions primarily due to fossil fuel burning (≈ 75%) and changes in land use (≈ 25%). Only about half of the emitted CO_2 remains in the atmosphere, where it affects the earth's radiation balance. The rest is partly dissolved in the oceans and partly taken up by the biosphere over land.

Measuring atmospheric carbon dioxide

Atmospheric measurements from the CO_2 surface network, consisting of about 100 stations, have been used to infer partitioning of CO_2 sources and sinks amongst oceans and land [e.g. Bousquet *et al.*, 2000; Gurney *et al.*, 2002]. These studies showed that the land uptake of CO_2, an

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Buchwitz, M.; Noel, S.; Bramstedt, K.; Rozanov, V. V.; Eisinger, M.; Bovensmann, H.; Tsvetkova, S.; Burrows, J. P. Retrieval of trace gas vertical columns from SCIAMACHY/ENVISAT near-infrared nadir spectra: first preliminary results. *Advances in Space Research*, 2004, **34**, 809-814.

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Gurney, K. R. [+ 25 co-authors]. Towards robust regional estimate of CO_2 sources and sinks using atmospheric transport models. *Nature*, 2002, **415**, 626-630.

IPCCC: Contribution of Working Group I to the Third assessment Report of the intergovernmental panel on Climate Change [Houghton *et al*. (eds.)] Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 2001.

Sabine, C. L. [+ 14 co-authors]. The oceanic sink for anthropogenic CO_2. *Science*, 2004, **305**, 367-371.

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contribution. Water vapour absorbs IR radiation but is not included in **Figure 1** because it rapidly equilibrates with the surface of the earth, especially over the oceans, so that its atmospheric concentration is determined largely by temperature rather than emissions strengths. However, it does provide an important positive climate change feedback. As the temperature rises, its atmospheric concentration will increase with a consequent increase in its IR absorption.

Ozone formation in the troposphere – regional chemistry and photochemical smog formation

Figure 1 shows that ozone is also a GHG and provides a direct link with air quality. Ozone is a major target of air pollution mitigation strategies, because of its effects on respiration and on ecosystem health. It is a secondary pollutant, formed from reactions involving NO_x

A potential problem that has been identified, though, is that reducing the concentration of aerosols in the troposphere, in order to improve air quality, could lead to warming of ~1 °C (Brasseur and Roeckner, 2005),

it is difficult to obtain the necessary information to make such an integrated environmental impact assessment. For example although it is generally accepted, on a g CO_2 emitted / km travelled, that diesel vehicles are more fuel efficient than petrol vehicles, this assessment does not take into account, for example, energy consumption differences in the refinement process. A full fuel cycle analysis is needed to make a relia

vapour levels in the troposphere with increasing temperature.

Figure 1: *Scatterplots of the change in global mean methane concentrations with global water mass and global mean OH levels. The data have been detrended and scaled so that they lie on the same axes. The units are arbitrary.*

If water vapour levels rise, the production of hydroxyl radicals from the excited state oxygen atom (O*) is likely to increase. The oxidation rates of methane and carbon monoxide will also proceed more quickly, owing to the higher production rate of hydroxyl radicals. To investigate this feedback, a

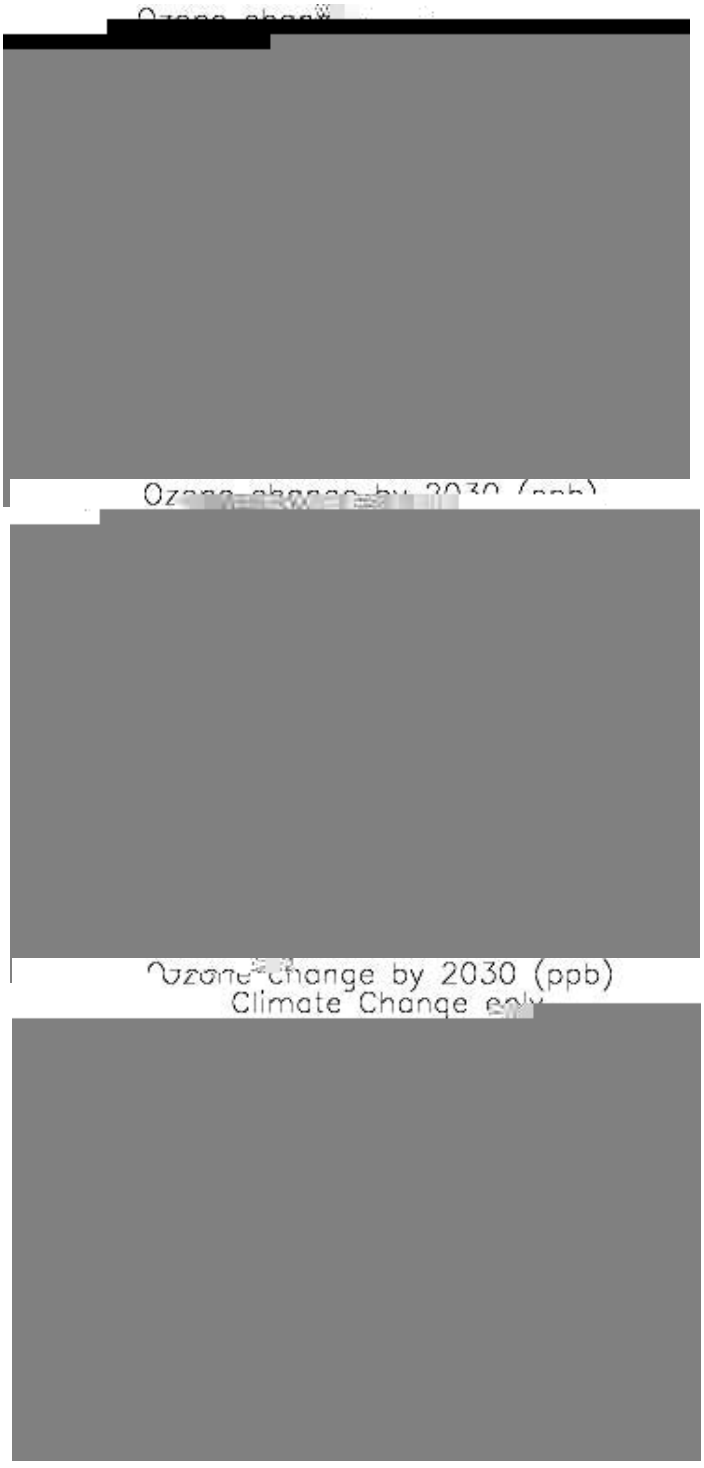

Figure 2: *Projected change in annual mean surface ozone levels between 2000 and 2030, using estimated emissions for 2000, and the Cu*

Summary

The levels of methane and ozone in the troposphere are closely linked via chemical reactions involving water vapour. Experiments using a coupled chemistry-climate model have shown that global methane levels are correlated with global water vapour levels, and global OH levels. Larger water vapour levels result in increased production of OH levels, and consequently smaller methane levels.

Further simulations using the coupled chemistry-climate model were used to study the effect of climate change on projected surface ozone levels for the year 2030. The water vapour levels are larger in the 2030 climate than in the 2000 climate. Climate change has reduced the projected ozone levels by 1 – 2 ppb over most of the globe. This reduction is due to the reaction between water vapour and excited state oxygen atoms. Owing to the increased water vapour levels, more excited state oxygen atoms react with water vapour, and fewer are quenched to the ground state to reform ozone. Hence, more hydroxyl radicals (OH) are made at the expense of ozone molecules, and ozone levels fall.

References

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Dentener, F., Stevenson, D., Ellingsen, K., van Noije, T., Schultz, M., and co-authors. 2006. The global atmospheric environment for the next generation. *Environ. Sci. Technol.*, **40**, 3586-3594.

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report of the intergovernmental panel on climate change (eds. J. T. Houghton, Y. Ding, D. J. Griggs, M. Noguer, P. J. van der Linden, X. Dai, K. Maskell,

(N). Here, we investigate potential future ozone changes from anthropogenic emission changes, changes in meteorology, and climate change induced natural emission changes of isoprene and soil-NO_x. We assume twice present-day CO_2 loadings to represent a future climate (2100).

Figure 1a shows that modelled annual mean surface O_3 for 2000 varies between 40-50 ppbv over large parts of Europe, Asia and North America as a direct result of emissions of O_3 precursors. The background O_3 levels are from 15 ppbv to 25 ppbv with the year-round low values in Central Pacific Ocean. Tropospheric O_3 is not only produced in the source regions of its precursors but it is also transported to remote oceanic regions under favourable meteorological conditions. For example, the elevated O_3 levels in the northern Pacific Ocean are the result of transport of pollutants from Asia.

Figure 1b shows changes in surface O_3 between 2000 and 2100 assuming only changes in anthropogenic emissions, i.e. with unchanged climate. The background O_3 levels are calculated to increase 10-15 ppbv by the end of this century based on the A2 emission scenario. In the Northern Hemisphere (NH), over 30 ppbv of O_3 increases are calculated over polluted continents. The largest annual averaged O_3 increases (over 40 ppbv) occur in Asia. The peak ozone concentration is calculated to reach 50 ppbv in summer months. For these regions, rapid economic growth and a population increase are predicted and can lead to an unacceptable air quality.

Increased surface emissions of O_3 precursors not only contribute to O_3 formation in source regions but also increased O_3 levels in remote regions through long-range transport. Vertical profiles of tropospheric O_3 in the year 2000 and the ΔO_3 (2100-2000) are shown in **Figures 2a & 2b**. The Figures r1Tc0.443evb0.33.8825 n4(a)1 3c5O

Figures 2a, 2b & 2c: *Annual and zonal mean tropospheric O_3 profile for 2000* ***(a)****; φO_3 (2100-2000) due to anthropogenic emission changes* ***(b)****; and φO_3 due to climate change only* ***(c)****. Units in ppbv.*

Ozone destruction in the source regions is associated with increased ozonolysis by isoprene; this signal then propagates to higher altitudes. On the other hand, we obtain elevated ozone

More on atmospheric hydroxyl radicals

A note from **Dwayne Heard** on the *commentary* by P. O. Wennberg, "Radicals follow the Sun", *Nature*, 13th July 2006, vol. 442, p. 145 and the *paper* by F. Rohrer and H. Berresheim, "Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation", *Nature*, 13th July 2006, vol. 442, p. 184.

The hydroxyl radical, OH, is the atmosphere's detergent, removing unwanted emissions and controlling the concentration of almost all trace gases. It has a short lifetime in the atmosphere, less than a second, and its concentration is extremely small (less than 1 part in 10^{13} mixing ratio), yet it is important to measure, as OH embodies the ability of the atmosphere to process emissions. There has been a worldwide effort by a handful of groups to au

Forthcoming symposium

Environmental Chemistry in the Polar Regions

Royal Society of Chemistry Environmental Chemistry Group

2007 Distinguished Guest Lecture & Symposium

A **one-day** meeting to be held in the Council Room at the Royal Society of Chemistry, Burlington House, on **Tuesday 6th March 2007**, from 10:30 am onwards.

The 2007 ECG Distinguished Guest Lecturer will be **Dr**

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Abstracts and biographical details of the speakers

Sediment records of environmental change in

Dr Anna Jones completed a numerical modelling PhD at Cambridge University before joining the British Antarctic Survey (BAS) in 1992. Dr Jones' initial research with BAS focussed on the stratosphere, but some years ago she moved closer to the ground to study boundary layer chemistry and exchanges between the air and the snow. Two seasons of field work have been completed in Antarctica, at the German research station, Neumayer, studying nitrogen chemistry and the production of NO

Fenceline monitoring: perils and pitfalls

Heightened awareness of environmental issues has led to an increased urgency in tackling problem areas of pollution. Fenceline monitoring is a technique for alerting industry about these problems. **Dr Kim Hampton** explains.

Introduction

New and existing environmental legislation coupled with a greater sense of corporate responsibility can assist in the protection of the environment. For UK industry, the most far reaching (and relevant) legislation to date is the regulatory framework within **Integrated Pollution Prevention and Control** (IPPC). IPPC is aimed at protecting the environment as a whole, taking into account emissions to air, water and land. The regulators, who are either the Environment Agency or a local authority depending on the activity, set permit conditions, i.e. the amounts of chemicals that are allowed to be released into the environment. These conditions are based in part on the implementation of Best Available Techniques (BAT), where the cost to the operator is balanced against the benefits to the environment.

The aim of IPPC is to prevent emissions and waste production, or at the very least reduce them to acceptable levels. If it is not practical to eliminate all the emissions to the environment, there is a need to monitor them to ensure permit levels are not exceeded. IPPC tends to be enforced at the exit point i.e. at the stack or effluent outlet. However, there are many emissions that cannot be tracked in this way, hence the need for **fenceline monitoring**. When fenceline monitoring is undertaken correctly, it is invaluable in assessing the gaseous pollutant emissions of a plant to the surrounding area.

A comprehensive monitoring scheme

Three types of open path systems are used, which measure along a 1 km light path and also evaluate meteorological conditions at the site. The remote sensing systems chosen were Fourier Transform Infrared (FTIR) Spectroscopy, Ultra Violet (UV) spectroscopy and Tuneable Diode Laser (TDL) Spectroscopy which measure 30 pollutant species, delivering data at 5 minute intervals continuously. Nine of the 30 chemicals measured are reported on a website (http://www.cchealth.org/groups/hazmat/fenceline/).

Summary

Fenceline monitoring is more complicated than just putting an instrument next to a fence or a boundary. Each site is different and has different requirements. Installations must be designed with care to obtain useful information and not to just generate numbers. It is important that along with measuring pollutants, complementary meteorological data are logged simultaneously. With increasing environmental legislation and an onus on caring for the enviro

Meeting report

The Investigation of Air Pollution Standing Conference

The Investigation of Air Pollution Standing Conference (IAPSC) was held at the NEC, Birmingham on Tuesday 5th December, 2006. More than 150 delegates attended, mostly from local authorities, but also representatives from Defra, the Environment Agency, monitoring and equipment consultants, academia and industry.

The subject of the morning session was ***particulate matter*** and was introduced by Richard Maggs (Bureau Veritas) with an overview of the 'UK Equivalence Programme for Monitoring of Particulate Matter', published by Defra in June 2006. The research compared a range of particulate monitors measuring PM_{10} and $PM_{2.5}$ at four locations representative of suburban, urban background, roadside and rural sites. Four of the monitors passed the equivalence testing without adjustment: Partisol 2025, FDMS (Filter Dynamics Measurement System) (PM_{10} and $PM_{2.5}$) and Beta SM 200; whilst the TEOM (Tapered Element Oscillating Microbalance), the principal monitor employed by the national AURN (Automatic Urban Rural Network), failed. Defra intend to retrofit the existing AURN TEOMs with FDMS units commencing January 2007. However, local authorities are advised that their own TEOMs may still be used with the 1.3 correction factor until they become due for replacement.

Dave Green (KCL) followed with his 'Practical and Technical Experience of using the FDMS Unit' at eight sites in London. The FDMS removes the need for the 1.3 correction factor applied to TEOM measurements by introducing a 'purge' filter to the process. Comparison studies of TEOM 1.3, FDMS and gravimetric monitors showed comparable background concentrations. However, at roadside

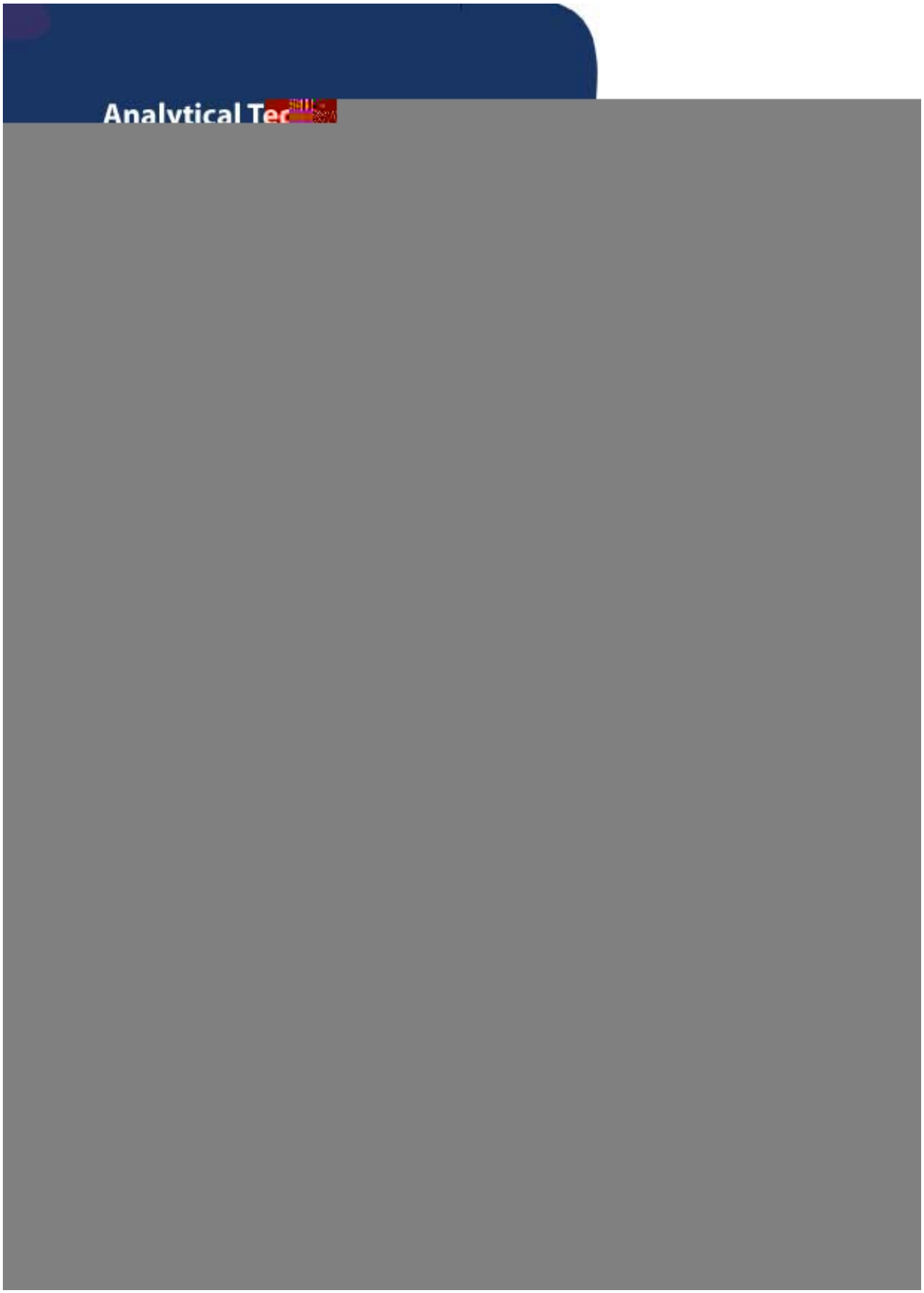
significant health impact. Transport and heating are the main sources of airborne particulates and measures to raise awareness and reduce the contribution from cars have been implemented, including 'car free' days and subsidising the retrofitting of filters to diesel vehicles. Despite these efforts, however, it is unlikely that Graz will meet EU guidelines and authorities are currently awaiting the new Euro5 Directive on emissions and exhausts.

Mike Woodfield (AEA Technology) concluded the morning session with his commentary on 'Sources of $PM_{2.5}$ in Europe' as detailed in the updated 'EMEP/CORINAIR Emission Inventory Guidebook – 2005' (http://tfeip-secretariat.org/unece.htm). It was observed that domestic combustion and municipal waste appear to contribute a greater percentage to $PM_{2.5}$ than PM_{10} but the contribution from agriculture is less.

The afternoon session focussed on ***social equity and air quality***, commencing with a social history of air pollution '50 years on from the Clean Air Act' from Peter Brimblecombe (UEA). The presentation concluded that although London no longer suffers the dense smogs of the 1950s – thanks in part to the measures introduced by the Clean Air Act 1956, but also due to changes in industry and social practices – the 'Big Smoke's' current health problems are now associated with traffic pollution.

This was followed by Ioanna Gegisian's (UWE) presentation of her PhD research examining 'Environmental Justice: What does it mean for LAQM?' This EA-funded project is looking specifically at Air Quality Management Areas (AQMAs) and deprivation indices, examining how social deprivation is addressed in Air Quality Action Plans (AQAPs). Through surveys, questionnaires and interviews with local authorities, Ioanna observed that social and wider economic impacts were the two least considered objectives in the selection process used to create Action Plans and that integration of AQAPs with other documents was hampered by a lack of communication between departments and incompatible deadlines.

Steve Moorcroft (Air Quality Consultants) spoke about the 'Exposure Reduction Approach and Implications


Analytical Ter

The RSC Virtual Library

A knowledge centre for environmental scientists

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There are hundreds of full text **e-books** in the **Referex**, **NetLibrary** and **Knovel** collections of the **RSC Virtual Library**. Examples of some titles related to the environment are:

REFEREX

Environmental Engineering
Features extensive in-depth coverage of risk analysis; biodegradation; the hydrologic cycle and water availability; noise pollution; collection of pollutants.

Handbook of Air Pollution Prevention and Control
Provides a concise overview of the latest technologies

Recent books on the environment and on toxicology at the RSC library

The following books and monographs on environmental topics, toxicology, and health and safety have been acquired by the Royal Society of Chemistry library, Burlington House, during the period July to December 2006.

An Introduction to Pollution Science

R. M. Harrison (ed.),
Royal Society of Chemistry,
Cambridge, 2006,
ISBN/ISSN: 9780854048298,
Accession No: 20060209,
628.52

Cobalt and Inorganic Cobalt Compounds