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CONTENTS

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A massive tabular iceberg adrift in the Weddell Sea off the Antarctic Peninsula. (Photo: British Antarctic Survey/C. Gilbert, PA). The disintegration of the 200-metre thick, 3,250 square kilometre Larsen B ice shelf into the Weddell sea in 2002 has been attributed to global warming. An understanding of the infra-red spectroscopy of carbon dioxide and water illuminates their relative roles as a greenhouse gases and in the causes of global warming (p. 5).

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(from March 2005)

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How microbial processes in estuarine sediments can control the mobility of technetium-99

Ian Burke, **Robert Mortimer** and **Katherine Morris** at the School of Earth and Environment, University of Leeds, together with **Chris Boothman**, **Francis Livens** and **Jon Lloyd**, at the School of Earth and Atmospheric and Environmental Sciences, University of Manchester, discuss how indigenous microbial processes in sediments can lead to technetium-99, a radionuclide present in radioactive wastes, being removed from solution and retained in sediments as hydrous TcO_2.

Introduction

Technetium-99 is a long lived (half-life, 2.13 x 10^5 years), β-emitting radionuclide that is significant in radioactive wastes. Under oxic conditions technetium is present as the pertechnetate ion (TcO_4^-), which is weakly sorbed to mineral surfaces and is one of the most mobile radionuclide species in the environment (1). By contrast, in reducing environments the lower valence forms of technetium (predominantly Tc^{4+}) form solid phases, and strong surface complexes with Al and Fe oxides and clays (2). Because of the long half-life of Tc, and its high environmental mobility, understanding the controls on how Tc is reduced and scavenged by sediments is essential to informing policy on how best to manage this contaminant. Within the natural environment, Tc is present at ultra-trace concentrations. This, combined with difficulties in its analysis, means that there is a paucity of environmental data for the radionuclide and little is understood of the solid phase interactions of technetium in the environment (3).

We used sediment microcosm experiments (Fig. 1) containing sediments uncontaminated with Tc from three different Humber Estuary sites. Sampling occurred with minimal disturbance so that the full indigenous microbial populations within the sediment remained in experiments (e.g. Fig 2). Microcosms were spiked with 1-5 μM TcO_4^-, and the behaviour of Tc and other redox indicator species were observed as progressive anoxia developed. By determining a range of redox indicator species, characterising the resident microbial community, and investigating the fate of Tc in these sediments, we were able to significantly increase understanding of the biogeochemical processes that have the greatest effect on Tc solubility in the natural environment.

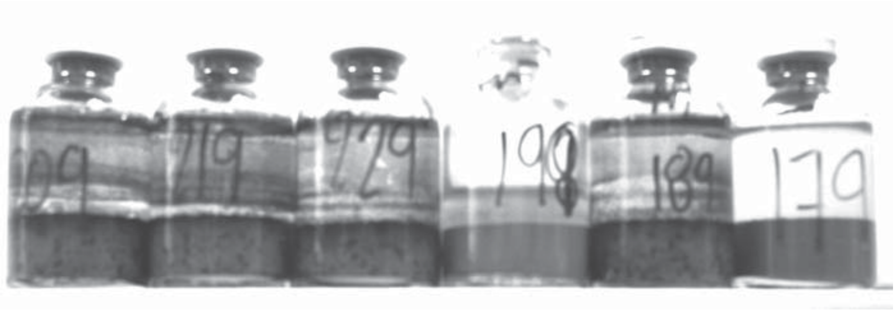

Fig. 1: Anaerobic microcosm experiments containing Humber Estuary sediments with; (from left to right) three Tc-amended experiments, an unsealed control, a non Tc-amended control and a sterilised Tc-amended control. All have been incubated at 10℃ for 40 days in the dark.

Results from anoxic microcosm experiments

In anoxic microcosms experiments, over 99% of Tc was removed from pore waters within approximately 20 days (Fig. 3). In sterile controls, however, Tc remained in solution as TcO_4^- indicating that Tc removal to sediments is a biologically mediated process. A classic cascade of terminal electron accepting processes (TEAPs) was observed and Tc removal occurred at the same time as active ingrowth of sediment bound Fe(II). At the concentrations used in these experiments, microbes are probably not able to directly utilise Tc as a TEAP (4), and Tc removal most likely occurs indirectly as a result of reaction with reduced species in sediments. Although sulfate reduction was observed in some experiments, it occurred after Tc removal was >99% complete. This indicates that microbial sulfate reduction was not an important factor in controlling Tc removal in these sediments (e.g. through the production of sulfide which can reduce and precipitate Tc). As Tc-solubility is not affected in experiments where nitrate or manganese reduction is the sole terminal electron accepting process (5,6), abiotic reduction of Tc(VII) onto solid Fe(II) containing-phases, formed as a result of bacterially mediated Fe(III) reduction, is therefore the most likely controlling mechanism for Tc-solubility in these experiments. This was confirmed in experiments where sterilised Humber

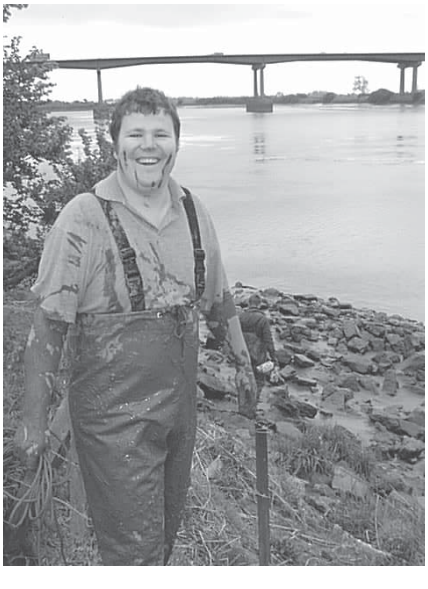

Fig. 2: Ian Burke shortly after sampling surface sediment from Humber Estuary mudflats at Boothferry. Care was taken to sample only the top few millimetres of the sediment surface. Face masks, gloves and sterile containers were used to protect samples (but unfortunately not Ian) from potential contamination.

Estuary sediments were inoculated with pure microbial cultures capable of either nitrate, iron or sulphate reduction. In these experiments Tc reduction only occurred in those sediments where the active accumulation of Fe(II) was detected in sediments as a result of microbial Fe(III) reduction.

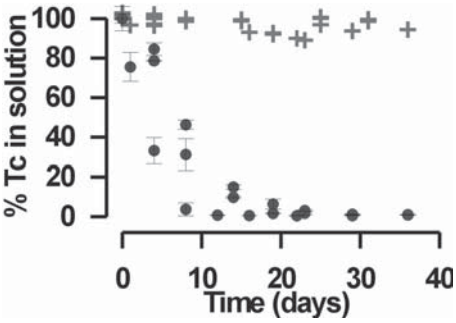

Fig. 3: *Time series of Tc-removal during an incubation of Humber Estuary sediments (•) amended with 5 μM Tc. Tc-removal does not occur in sterile controls (+) indicating a biologically controlled process*

Microbial community analysis

A combination of culture and DNA dependent techniques was used to determine the microbial community present during Tc removal and to assess how that community changed with time during anoxic incubation. Intergenic spacer analysis has been successfully used in other sediments (7) to 'fingerprint' changes in microbial communities, but in Humber Estuary sediments this technique showed that the microbial communities present at all sites were complex and closely related. In addition even though nitrate-, manganese-, iron- and sulfate-reduction were observed in a classic redox cascade order, no changes in community structure occurred over the same timescales. Analysis of a 500 b. p. region of extracted microbial 16S rDNA amplified using broad specificity PCR primers, typed by RFLP and sequenced, revealed a very complex clone library dominated by g-Proteobacteria. Bacteria related to organisms capable of a wide diversity of aerobic and anaerobic processes including known nitrate-reducing (*Rhodobacter sp.*), metal/sulfur- (*Pelobacter* sp.) and sulfate-reducing bacteria (*Desulfovibrio sp.*) were present. Therefore, even though the microbial population remained constant during microbial incubations, species were present that were able to switch to each TEAP in turn as it became the most energetically favourable mode of respiration. In an attempt to isolate the microbes capable of Fe(III) reduction, potentially the most important in mediating Tc reduction, 10% sediment inoculums were incubated in Fe(III) containing media and repeatedly sub-cultured. 16S rDNA analysis of this extracted culture produced a clone library dominated by *Shewanella* sp. This species when reintroduced to sterilised sediments was found to be able to mediated Fe(III) and Tc reduction in those sediments.

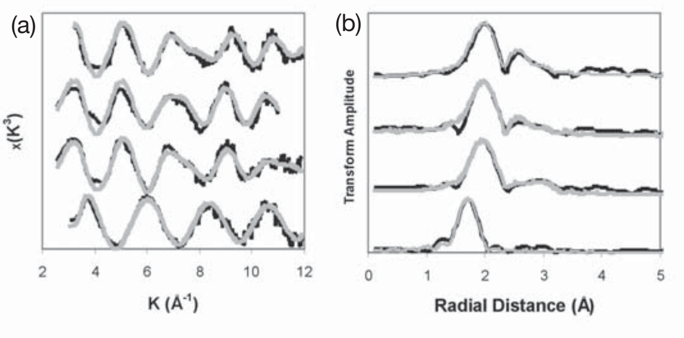

Fig. 4: *(a) k3-weighted Tc K-edge EXAFS spectra and (b) Fourier transforms of the Tc-labeled sediments used in the microcosm experiments of the following (bottom to top): solid pertechnetate standard (8); sulfate-reducing sediment amended with 1000 μM Tc; Fe(III)-reducing sediment amended with 1000 μM Tc; progressive anoxia, biotic sediment amended with 1000 μM Tc. The black lines represent experimental data and the gray lines represent the best model fit using Excurv98. All three reduced samples were most closely modeled by hydrous Tc(IV)O$_2$-like phases.*

Fate of Tc in sediments

The Tc-phase that sorbed to sediments was investigated using extended X-ray absorption spectroscopy fine edge structure analysis (EXAFS) at the Daresbury synchrotron light source. The detection limit constraints of EXAFS required a much higher Tc concentration than our previous experiments. Sediments undergoing Fe(III)- and sulfate-reduction, respectively, were amended with 1000 μM TcO$_4^-$. Under strictly anaerobic conditions, Tc removal occurred within 2 days due to abiotic reaction with reduced phases in those sediments. In addition, oxic sediments were also incubated anaerobically with 1000 μM TcO$_4^-$. Here, microbially mediated ingrowth of extractable Fe(II) was observed over a 6 month incubation period, and >99% Tc was removed from solution, representing one of the highest Tc concentrations known to have been reduced by naturally occurring microbial processes. The main features in the EXAFS spectra and Fourier transforms for all three samples are very similar (Fig. 4), and modeling produced good fits for all of the samples with an inner shell of six oxygen backscatterers at *ca.* 2.00 Å. This is consistent with the formation of hydrous Tc(IV)O$_2$-like phases (8), previously reported as microbial reduction products by other workers (6,9), and confirms that the removal of TcO$_4^-$ from solution was accompanied by the formation of hydrous TcO$_2$.

Implications for Tc behavior in the natural environment

In our anoxic incubation experiments, indigenous Fe(III)-reducing bacteria were stimulated when the reduction of metals represented the most energetically favorable TEAP, and Tc reduction was associated with the active accumulation of microbially generated Fe(II) in sediments. EXAFS demonstrated that Tc formed a hydrous TcO$_2$ phase within these sediments under both Fe(III)- and sulfate-reducing conditions. This implies that TcO$_4^-$ released to the environment will be scavenged to sediments by reductive precipitation to hydrous TcO$_2$ when active Fe(III) reduction is occurring or when it is exposed to Fe(III)- or sulfate-reducing sediments. Therefore, when TcO$_4^-$ is discharged into oxic environments, Tc reduction is apparently mediated by a potentially wide variety of microbes, and reducing sediments may preferentially accumulate Tc(IV) rather than diluting and dispersing it as TcO$_4^-$. This may be used to advantage in understanding the biogeochemistry of technetium in estuarine environments as well as in remediation of Tc contamination in a range of environments.

Acknowledgements

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A full report of this work – Effects of progressive anoxia on the solubility of technetium in sediments – appears in *Environmental Science and Technology*, 2005, **39**, 4109-4116.

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May 2005

Meeting report

Air Pollution 2005: Modelling, Monitoring and Management of Air Pollution

XIII International Conference on Air Pollution, Cordoba, Spain, May 2005

Based in the New Forest, the Wessex Institute of Technology (WIT) is a commercial enterprise focusing on publishing, conference organisation and software services for academia and industry. On May 16-18 2005, WIT organised the 13th International Air Pollution Conference at the Hotel Hesperia Cordoba, Spain. Presentations at this conference described the modelling, monitoring and management of air pollution, and the proceedings have now been published.*

The presence of 100+ delegates from 30 countries (ranging from the US, Chile, Brazil, and Canada to Europe, Korea, Japan, and Kuwait) reflected the interest of planners and legislators in air quality data and related legislation.

The opening paper "Micromixing effects in air pollution modelling" (Richardson, Cambridge) described methods by which air quality models (AQMs) can be improved to predict more accurately any significant variations in the concentrations of pollutant species that may occur over small distances. Related papers discussed modelling air quality emissions in cities (Santiago) and from industry (refineries and power plants). Air Quality Management sessions examined the provision of air quality data for local government and the public (e.g. Barnes and co-workers: "GIS mapping of NO_2 diffusion tube monitoring in Cornwall, UK"). Other topics included: urban air pollution, modelling and monitoring; cross channel pollution; and biogenic volatile organic compounds.

Other noteworthy contributions at the conference included:

- Elmi and co-workers (Bologna): "A low-cost transportable instrument based on microsystem technologies for benzene monitoring in outdoor air". The instrument is planned for production in 2006 at a cost of around £7K. The apparatus has a detection limit of 0.2 ppb with hourly reporting, self-calibration and an in-field unattended lifetime of 6 months. It would be a welcome simplification of the cumbersome and complex array currently used for benzene monitoring.

- Al-Rashidi (Loughborough): "Air quality modelling of sulphur dioxide emission from power plants in Kuwait". The conclusion of this paper was a clear recommendation for the optimum sulphur content of the fuel used in the power plants. But it was the successful use of the US-EPA approved ISCST3 model (industrial source complex model for short-term prediction) to quantify the impact of SO_2 release which was of interest. The relatively uncomplicated terrain and meteorology together with well-defined emission sources made this a good case study for the application of the ISCST3 AQM.

- Stewart and Andino (Florida): "Studies of the uptake of gaseous ethyl 3-ethoxypropionate onto ammonium sulfate and ammonium nitrate aerosol particles". Work on the uptake, loss, and transport, of organic species by atmospheric aerosols that highlighted the importance of such heterogeneous interactions in the troposphere.

- Kretzschmar (Flemish Institute for Technological Research): "Greenhouse gas emissions in the EU: are we reaching the Kyoto objectives?" An update of Kyoto protocol compliance by the 15 EU member states, which suggested that the set targets may be difficult – though not impossible – to achieve by the 2008-2012 deadline.

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* Brebbia, C. A. (Ed.), *Air Pollution XIII*, WIT Press, Southampton, 2005. ISBN 1-84564-014-4. Volume 82, *WIT Transactions on Ecology and the Environment*. http://library.witpress.com/pages/listBooks.asp?tID=4

Global warming: the physical chemistry

Despite the widespread scientific consensus, and the partial political agreement that global warming is a serious problem which is largely man-made, there are doubters. These range from newspaper columnists who make a virtue of scientific ignorance, web pundits and even novelists, to (a few) serious climatologists who dispute subtle aspects of the modelling. In between, there seem to be some puzzled chemists, and even a few sceptical ones. **Professor Robert Lloyd**, formerly of Trinity College, Dublin, describes how the infra-red absorption spectra of carbon dioxide and water explain their relative importance as green-house gases and as contributors to global warming.

This article is an attempt to clear up some common misconceptions which arise at the relatively low level of the basic physical chemistry/physics of the infra-red (IR). In this area, we chemists may be at something of a disadvantage because of our training. We are very familiar with a part of the total IR spectrum, but the "group vibration" region, about 4000 - 1000 cm^{-1} (2.5 - 10 μ), is not the region of greatest importance to global warming effects. Furthermore, we have all been taught not to put too much material into our mulls or solutions; if we do, the beautiful sharp peaks turn into ugly flat-topped objects, since saturation is occurring. Such saturation is very important in understanding what is going on in global warming.

Much of the radiant energy from the sun, which approximates to a black body at 5780K, is transmitted well by the atmosphere, which is almost transparent in the visible and near-visible regions. About 30% of this radiation is reflected, mainly by clouds, and the rest warms Earth so that it too radiates, approximately as a black body. The incoming and outgoing energy reach an equilibrium position, determined by our distance from the sun. (Partial black body curves for various temperatures are shown in Figures 1 and 2). (Note 1).

In the absence of any absorption of the outgoing energy, the average equilibrium temperature of our planet would be 255K. Thus nearly all the surface of the planet would be expected to be well below the melting point of ice, so that it is at least questionable whether or not life, dependent on liquid water, could have followed the path we know (Note 2), without the additional warming which gives us the current average temperature of about 288 K.

Much of this additional warming comes from absorption of the outgoing radiation by atmospheric water vapour. Although water has strong IR absorption in the "group vibration" region, the most significant energy absorption is from the very strong and complex *rotational* structure between *ca.* 1 cm^{-1} and *ca.* 700 cm^{-1}. The upper part of this region overlaps with the lower frequency region of the outgoing 288K black body spectrum, so that much of this energy is absorbed in the atmosphere, and then re-radiated (Note 3). Because some of this re-radiated energy is returned to earth, the net radiation reaching the surface is greater than it would be with no atmospheric absorption, and the surface temperature rises. However, obtaining quantitative estimates of the warming due to this is far from trivial. The first point to make is that there is a positive feedback effect – as the temperature rises, so does the saturation vapour pressure of water, so more water enters the atmosphere, and this produces more warming. However, not all the atmosphere is saturated (Note 4) with respect to water, so quantifying this is complex; solar reflection by clouds, the variation of cloud cover with water content, and atmospheric convection, also have to be included. Current estimates give a warming contribution due to water alone of about 20K, and about half of this comes from the "feedback" effect (Note 5).

This only accounts for two-thirds of the total warming (about 30K). The rotational absorption intensity of water falls off rapidly above about 500 cm^{-1}, as the population of rotational levels decreases following the Boltzmann distribution. Thus the higher frequencies of the black body emission are transmitted – there is a "water window" in the atmospheric absorption which reaches up to about 1200 cm^{-1}, where the first of the water vibration-rotation bands, associated with the bending vibration, begins. The lowest (bending) vibrational band of carbon dioxide fits into the lower frequency region of this window, and this accounts for most of the rest of the warming. Thus the "natural" or "primary" greenhouse effect is a sum of the effects of water and the natural background of about 280 ppm of CO_2, with some smaller contributions from other sources (including ozone, which absorbs close to the centre of the window). For many centuries the level of CO_2 was constant, as can be seen in ice-core measurements, but since about 1800 it has been increasing, and the rate of increase has also increased, giving a current (2003) level of about 375 ppm. It is the additional warming above the natural level, due to emissions from human activities, which is commonly referred to as the "greenhouse effect".

Figures 1 and 2 illustrate some of these points (Note 6). Figure 1 is the IR emission from Earth, measured above the atmosphere at a particularly dry position – the Sahara. The Earth black body curve can be seen in the atmospheric ("ATM") window at position C; this is being emitted from ground level. Most of the rest of the rest of the spectrum is that emitted by molecules within the atmosphere. Even in this "dry" spectrum there is a lot of water emission below 700 cm^{-1} and above 1300 cm^{-1}, but since the emission is not saturated, individual components (Note 7) show as sharp peaks. This radiation comes from several km high in the atmosphere (see the right-hand graph in Fig. 1), where the temperature is much lower. The most prominent feature in the spectrum is the very strong CO_2 feature from about 550 cm^{-1} to 800 cm^{-1}. The broad "flat-topped" nature of the centre portion of this spectrum contrasts with the sharp peak, due to the Q branch, which is shown in most textbook (absorption) spectra. This is the result of saturation: not only is the Q branch saturated, but so are most of the wings of the adjacent P and R branches, and everything in between; in this saturated region the emission matches the high-altitude black body curve at about 218K. This energy, originally emitted at the surface, has been absorbed and re-emitted several times through successively cooler regions. The "missing energy" between the 218K and 320K curves has been returned to the surface. The spectrum also shows the re-emission of radiation absorbed by ozone in the upper atmosphere, about 2-3 km altitude, and by methane (see below).

Figure 2 shows the converse situation – a ground-based spectrometer is "looking upwards" at the downward emitted radiation, but now with more normal humidity, so most of the water emission at wavenumbers below 550 cm^{-1} is at saturation, and this comes from a low altitude, temperature about 275K. Again the very intense emission between 650 cm^{-1} and 750 cm^{-1} is due to atmospheric CO_2. CO_2 emission is therefore returning much of the radiation emitted from Earth over a fairly wide slice, close to the maximum of the spectrum of black body radiation (Note 8).

The effects of increasing the CO_2 level are not simple. It might be thought that once there is enough of any "greenhouse gas" in the atmosphere for saturation to have been reached, absorption of radiation is complete, so there could be no more warming, but this is not so. Firstly, the saturation only applies to the centre region. At the wings, increasing concentration increases the number of photons absorbed, and returned to earth. Furthermore, there is still a warming effect at the surface due to the centre of the band, because the first absorption now takes place at a lower altitude, where the temperature is higher. This energy is re-emitted, and more energy is returned to the surface. However, this is a very non-linear effect – the warming is not directly proportional to the number of molecules added, but rises more slowly. It needs to be emphasised, in view of certain media comments, that the warming effect from CO_2, both natural and anthropogenic, is amplified by the water feedback mechanism, as the effect of water itself is (see above). Far from "ignoring water as a greenhouse gas" as some pundits proclaim, workers in climate modelling build this effect in to all their models. This amplification of the CO_2 warming effect by water is responsible for the predicted substantial warming over the next century or so, with all the very serious consequences.

Other "greenhouse gases", though present in much smaller amounts, make appreciable contributions because they absorb in the remaining window region where neither CO_2 nor H_2O absorb very strongly. Methane is significant now, but may have been catastrophic in the past. A major change in the ancient history of the Earth has been associated with warming following the decomposition of the methane-water clathrate (Note 9), and large amounts of this are known to be present now. The methane absorption band can be seen in Figure 1, though in Figure 2 it has been lost in the overlapping of the traces of many water lines. This absorption is currently well short of saturation, so warming effects are approximately linear in the number of molecules added, and per molecule, methane is about 50 times more effective than CO_2, at least in the short term (upper atmosphere chemistry slowly destroys methane). As a result, methane from agriculture can be a large component of total greenhouse emissions for countries, even in the developed world, for example Ireland and New Zealand. Nitrous oxide and halocarbons also contribute to the total. As a result, despite the small concentrations of these minority species, their heating effects taken together are more than one-third of the total effect from man-made greenhouse gases (Note 10).

Clearly the "greenhouse effect" is a very intricate subject, and this short note has only attempted to deal with the very beginning of the complex process which generates climate. I hope it has been of some help, and the further reading listed below should allow access to the vast amount of real data and explanation which is available.

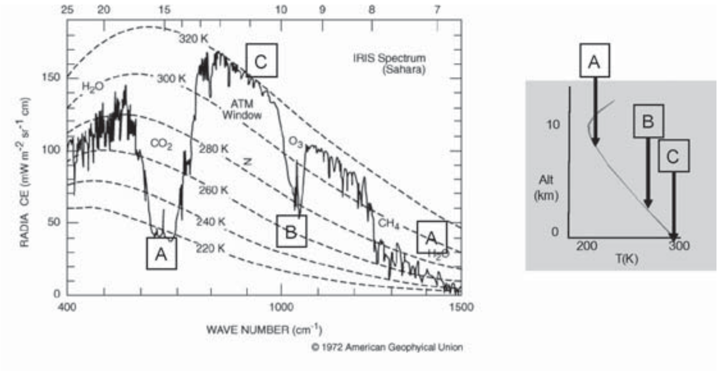

Figure 1: *Infra-red emission spectrum from Earth, taken at high altitude over the Sahara (Copyright American Geophysical Union). The letters on the spectrum indicate the approximate altitudes and temperatures for particular emission features: see the curve in the right-hand section. The dashed lines show the energy distributions for a black body at various temperatures.*

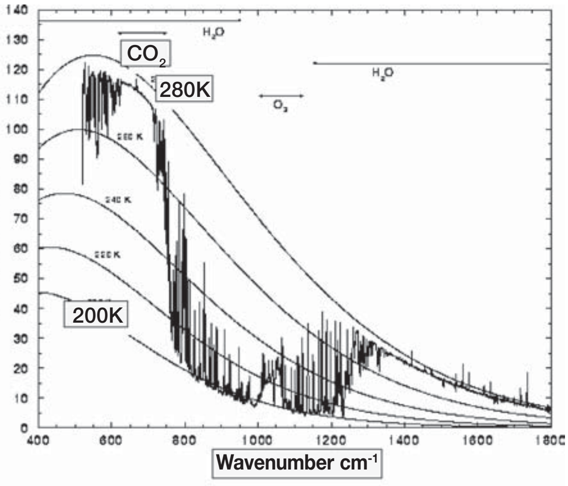

Figure 2: *As Figure 1, but now on a ground-based spectrometer recording emission to Earth from the vertical column of the atmosphere, with a higher water content than in Figure 1. (Modified from a version provided on the ESPERE website).*

Notes

1 These are plotted as energy density per wavenumber on a horizontal scale linear in wavenumbers. Many physics texts show curves linear in *wavelength*, and on these the maxima occur at different positions.

2 It is also of great importance to life that one part of the solar emission *is* absorbed significantly by the atmosphere, the hard UV radiation, which is removed by ozone.

3 In addition, there is a component from the "water bend" vibration, but there is not much of the total energy of the black body emission at these higher frequencies.

4 Unfortunately, the word "saturation" is used both for the SVP and for infrared absorption, though there is no necessary connection between these uses. In the rest of this note, the word refers to saturation of IR absorption.

5 See IPCC, referenced in "Further information", Technical summary, D.1 Climate Processes and Feedbacks.

6 A more dramatic version of Figure 2, in which the "window" is emphasised by colouring various sections, can be found at: www.espere.net/Unitedkingdom/water/uk_watervapour.html#x3. Similar spectra, obtained under different conditions can be found at: http://cimss.ssec.wisc.edu/aeri/science/aeriret/

7 The rotational structure is very complex, and many of the apparent peaks in the figures consist of several components.

8 Since the intensities at saturation are controlled by temperature, the emission envelope follows a black body curve, and information about atmospheric temperature profiles can be extracted from such spectra; see the links in note 6.

9 "However, these deposits are enormous, about 10^7 TgC, and there is an indication of a catastrophic release of a gaseous carbon compound about 55 million years ago, which has been attributed to a large-scale perturbation of CH_4 hydrate deposits"; see IPCC Climate Change 2001: Working Group I: The Scientific Basis 4.2.1.1.

10 See IPCC: Climate Change 2001: Working Group I: The Scientific Basis 6.3.4

Further information

This article has to some extent followed the approach in A. P. Cox, "The Elements on Earth" (Oxford 1995), pp 14-19, with some amplification. IR spectra of the various molecules mentioned are available (at medium resolution) at http://webbook.nist.gov/chemistry/

Various other websites give some details on the stages by which the spectroscopic information is turned into models of the climate of the earth; one of the most detailed, which nevertheless is well-organised into links, so that particular interests can be followed through, is at http://www.aip.org/history/climate/index.html

As an introduction to this, there is a spectacular demonstration of the way in which global temperature and CO_2 levels have tracked each other over 160,000 years at http://www.aip.org/history/climate/xVostokCO2.htm

A site which attempts to answer individual problems is www.realclimate.org/index.php?p=1

There is a large, somewhat indigestible but authoritative collection of documents from the Intergovernmental Panel on Climate Change (IPCC) at http://www.grida.no/climate/ipcc_tar/index.htm

Within this the most directly relevant material to this note is the discussion of carbon species at http://www.grida.no/climate/ipcc_tar/wg1/095.htm and of the effects of the absorbed radiation at http://www.grida.no/climate/ipcc_tar/wg1/212.htm

Acknowledgements

I am particularly grateful to Professor Norman Sheppard, who provided advice at an earlier stage of this manuscript, and to Dr. Rob Jones of the Chemistry Department, University of Cambridge, for a detailed discussion, and for making Figure 1 available. Any remaining errors are my responsibility. I would also like to note the contributions of two Skeptical Chymists, who in extensive correspondence have forced me to clarify my own ideas on this topic.

Biographical note

In 2000, **BOB LLOYD** retired from the Chair of General Chemistry at Trinity College, Dublin, where he had helped to set up a new course in Environmental Chemistry. His research, (after a start in solution kinetics) has been mainly in photoelectron spectroscopy and allied methods, initially in the gas phase (at the University of Birmingham, to 1978) and later in angle-resolved form on surfaces, particularly with adsorbed molecules.

Advances in surveying the soil chemistry of UK urban environments

Barry Rawlins and **Kirsten O'Donnell** from the British Geological Survey (Keyworth, Nottingham) describe their work on urban soil analysis.

Introduction

The soil acts as both a sink (repository) and source for contaminants in urban environments. Diffuse pollution is widely perceived to account for a significant component of the contamination of urban soils in the UK. But just how significant is diffuse pollution? How can its magnitude be assessed in a complex and ever-changing environment? How can we account for the presence of hotspots of contamination? Does the contamination we measure in the soil agree with our expectations given the distribution of historical land use in the urban area?

The British Geological Survey, as part of its GSUE (Geochemical Surveys in Urban Environments) project has begun to answer some of these questions. This is part of fulfilling BGS's role: the acquisition of geoscience knowledge and information (*via* surveying, monitoring and research), its interpretation, management and dissemination. Since 1993, more than 7000 individual soil samples have been collected from around 20 urban centres (see Figure 1). The samples have been analysed for their inorganic chemical composition, including a range of trace metals that are also persistent contaminants. These data are frequently provided to consultants, local authorities and researchers for a variety of applications. The excess sample from each sample is archived and linked *via* a unique sample number to an electronic database, which retains useful information about the sample, including its location and land use.

Point and diffuse pollution

We recently undertook a study on the soil chemistry data from Sheffield consisting of 569 sample locations. We used advanced spatial statistics to identify those sites, which represent sites of hotspots of contamination. They have unusually high concentrations in relation to neighbouring sample locations. Figure 2a shows a smoothed map of Cr concentrations across the City; the sites hotspots of contamination are shown as black dots. The smoothed map in Figure 2b was created with these hotspots removed and gives a more accurate representation of the background process combining the natural soil chemistry plus a component of diffuse pollution. The highest soil Cr concentrations in both maps occur to the north-east of the City. This accords with its widespread use in steel manufacturing which has historically been sited in this part of the City. Statistical analysis showed there was an association between historical land-use, based on Ordnance survey maps, and Cr hotspots.

One way to estimate the amount of diffuse pollution in urban soil is to compare them to a series of soils in rural areas that developed from the same parent material. Sheffield is well suited for this as it positioned in the middle of a widespread rock type referred to by geologists as the Coal Measures. We also have soil chemistry data for soil samples developed from the Coal Measures in rural areas. We first removed the hotspots from the urban dataset and then compared the median values (a robust measure of the centre of a distribution) from the urban and rural soils for three elements: lead, chromium and nickel. We believe that a substantial difference between the median values provides an estimate of historical diffuse pollution. The difference for lead was substantial; the urban median (203 mg kg^{-1}) was twice the rural median (101 mg kg^{-1}). At this stage we cannot comment on the relative magnitude of the different sources, but historical use of leaded petrol may be one of a number of significant contributors. The differences for chromium and nickel were more modest – increases of 14 and 25% respectively. To our knowledge this is the first attempt to estimate diffuse pollution in urban soil in the UK. This work is presented in more detail in a forthcoming paper in Soil Use and Management (Rawlins *et al.*, in press).

Figure 1: *Urban centres surveyed by BGS between 1993 and 2005.*

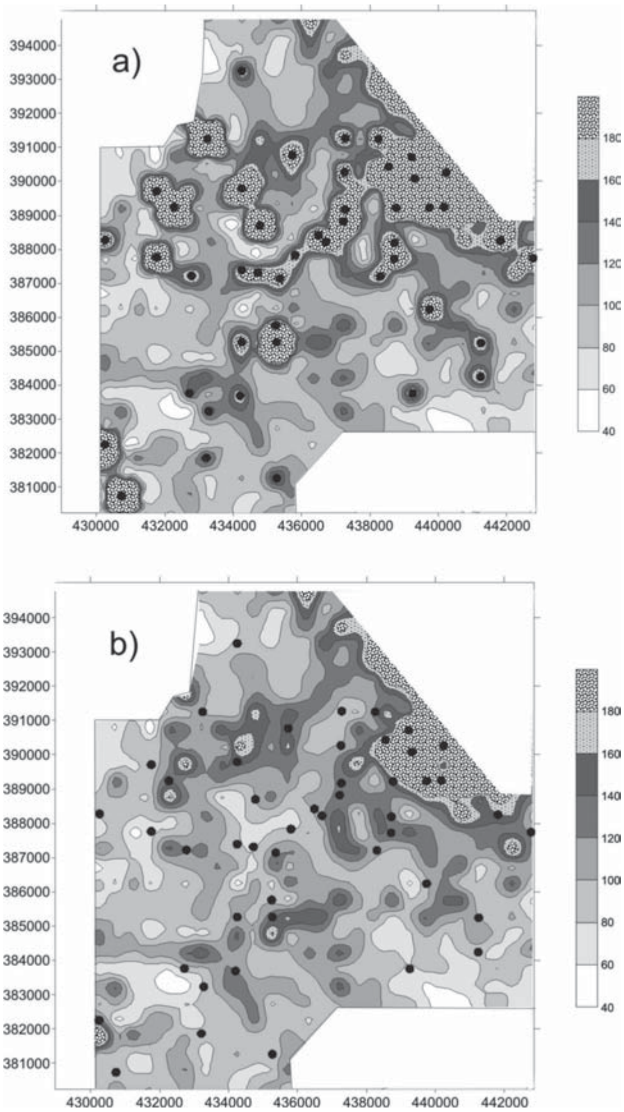

Figure 2: Contour map of Cr concentrations in the soils of Sheffield: a) including contaminant hotspots (•), and b) without contaminant hotspots (•) used for interpolation

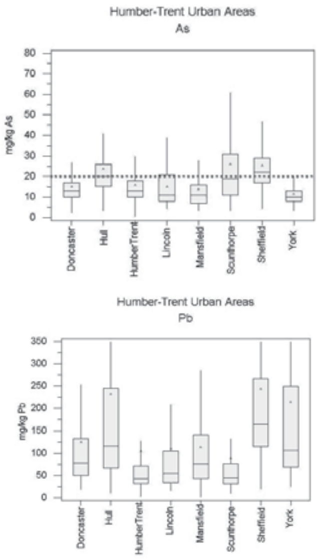

Figure 3: Box and whisker plots of soil a) arsenic (As) and b) lead (Pb) concentrations in the topsoil (0-15 cm depth) in various urban centres and the rural soils of the region (Humber-Trent)

Comparison between urban centres

The BGS has soil data covering rural areas, as well as seven urban centres across the Humber-Trent region. This is a unique soil geochemical dataset enabling comparison of closely distributed UK urban centres with the regional baseline. One of the main applications is improving our understanding of the nature of urban soil geochemistry, which may vary between urban areas as a result of differences in industrial history, transportation and underlying parent material types.

Figures 3a and 3b illustrate features of the distributions of arsenic (As) and lead (Pb) respectively in the seven Humber-Trent urban areas and in the non-urban land (labelled Humber-Trent). The lower and upper ends of the boxes represent the 25th and 75th percentiles, the line is the median and the cross is the mean of the data. The dotted line in Figure 3a represents the soil guideline value (SGV) for As in soils of residential land use (20 mg/kg). The SGV for Pb (450 mg/kg) is outside of the range shown in the box and whisker plot (Figure 3b). Elevated levels of As in the urban soils of Scunthorpe and Sheffield, with respect to the regional distribution and the SGV can be attributed to the location of these urban areas over the Frodingham Ironstone and the Carboniferous Coal Measures, respectively, which are both enriched in a number of trace elements, including As. The exploitation of coal around Sheffield may also have contributed to elevated concentrations of trace elements in the urban soils.

Elevated levels of As and Pb occur in the soils of Kingston-upon-Hull relative to the regional baseline. The latter may in part be related to the former operation of a metal smelter to the west of the city. Although the levels of As in the other urban areas approach the SGV, exceeding it in some cases in the upper ranges, they are fairly consistent with the regional distribution. This suggests that As is naturally elevated in the soils of the Humber-Trent region as a whole. Although the concentrations of Pb in the Humber-Trent urban soils are predominantly below the SGV for residential areas involving plant uptake, the skewed distributions, with strong deviations of the mean values from the medians, are indicative of anthropogenic, point contamination.

Acknowledgement: We would like to thank **Dr Murray Lark** (Rothamsted Research) for his contribution to the geostatistical analysis of the Sheffield data.

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British Geological Survey http://www.bgs.ac.uk/

Changes in soil metal content after addition of compost

Dr Maria Concepcion Ramos from the Department of Environment and Soil Science, University of Lleida, Spain, describes the potential environmental hazard of changes in metal concentrations of a vineyard soil from adding composted organic waste.

Introduction

The application of composted organic wastes to improve soil physical characteristics is a common practice in agricultural land – although in some cases this is a means of recycling high quantities of waste generated from intensive animal production. These residues improve soil physical properties by increasing soil organic matter content, and producing an enrichment of soil nutrients in a readily utilizable form. However, the composts usually contain trace elements, which at moderate levels can be beneficial for the soil, but might have a negative effect at higher concentrations. Most of the elements added to soils with compost are immobilized in the soil by chelation with organic matter and by adsorption on clay minerals; they are precipitated as insoluble compounds, and usually accumulate in the upper soil layers (Yaron *et al.*, 1996).

The determination of total metal content in soils is important in order to understand how the levels could increase as a result of agricultural practices. However, the toxicity of metals depends not only on the total concentration but also on metal mobility and reactivity. The most common way to analyze metal mobility is by using extractants. Although there has been much effort to harmonize and standardize analytical methods, there is no reference method at present for determining each fraction. Chelating extractants such as EDTA (ethylenediaminetetraacetic acid) and DTPA (diethylenetriaminepentaacetic acid) have been extensively used (Ure *et al.*, 1993; Brun *et al.*, 2001, Marcet *et al.*, 2003). Other authors advocate the use of neutral salt extractants (Gupta and Aten, 1993; Bucher and Schenk, 2000; Keller and Hammer, 2004).

The power of the extracting method depends on the soil characteristics. DTPA was first developed for calcareous soils (Lindsay and Norvell, 1978) and is suitable for neutral to alkaline soils (Hammer and Keller, 2002). Zhang and Shan (2000) found that DTPA extractants represented a highly available metal ion fraction of the total metal content. Brun *et al.* (2001) showed a good correlation between the DTPA extractable fraction and metal accumulation in root maize grown on Cu contaminated soils. Pinamonti *et al.* (1999), in a study on the use of compost in viticulture, pointed out that the concentration of heavy metals in plant tissues was positively correlated with the DTPA-extractable form of the metals in the soil, but was not correlated with the total or the EDTA-extractable forms. Other authors use a sequential extraction method to analyse the different fractions in which the element is found (Tessier, 1979).

In this study, changes in metal content resulting from the application of composted cattle manure to a calcareous soil were evaluated. Copper and zinc, the metals in higher proportion in the applied residues, were analysed.

Material and methods

Soil sampling

Samples were taken from a vineyard soil, which had undergone alterations to its soil profile before vineyard establishment some 12 years ago. The characteristics of the soil are shown in Table 1. In order to improve soil properties, composted cattle manure was applied at a rate of 40 Mg ha^{-1} in alternated rows, and mixed in the 25-cm upper layer. Soil sampling was carried out one year after compost application in areas with and without compost and at 4 positions in the plot slope. Soil samples were dried and sieved using a 2-mm mesh.

Extraction procedures

Copper and zinc were analyzed in each soil sample. A simple extraction method was performed in order to evaluate total metal content in the soils (digestion with an acid mixture: 2.5 mL 65% HNO_3, 7.5 mL 37% HCl, and 2.5 mL deionised water).

The extractable metal fraction was evaluated using DTPA (0.005 M diethylenetriaminepentaacetic acid, 0.1 M triethanolamine, and 0.01 M ammonium acetate at pH 7.3). The sequential extraction procedure proposed by Tessier (1979) was used to analyse the different forms: exchangeable, the carbonate fraction, the fraction bound to Fe and Mn oxides, the fraction bound to organic matter and the residual fraction. Blank samples were prepared according to each procedure and the concentration of the extracts was corrected by subtracting the corresponding blank concentration. All material was cleaned by soaking in 10% HNO_3 (v/v) and then rinsed with purified water. Metal concentrations were measured by atomic absorption spectroscopy. Two replicates of each analysis were carried out, and the average value is reported.

Results

The analysed soils have relatively high silt (40-45%) and sand contents (43-51%), but low clay contents (8-12%). Calcium carbonate content is relatively high ranging from 20 to 38%. The pH is 8.5 on average. The electric conductivity showed values between 0.17 and 0.19 dSm^{-1}, and the organic matter content was low (< 1%), changing significantly after compost application.

The average value of total Cu was 37 mg kg^{-1} in the untreated soils and about 43.6 mg kg^{-1} in treated soils, without significant differences (Table 2). The Cu DTPA-extractable fraction increased after compost application from 5.8 to 8.1 mg/kg, which represented 15% and 18% respectively of the total metal content. From the sequential analysis, the fraction linked to the organic matter increased from 22.9% to 29.5%, decreasing the residual faction, although the latter was still more than 64%. The DTPA extractable fraction correlated with the fraction linked to organic matter, but the correlation was not significant at 95% confidence level and there was no correlation with other fractions.

The average total Zn content increased from 59 to 69 mg kg^{-1} after the application of compost (Table 2), although individual values near 80 mg kg^{-1} were also observed. The Zn DTPA-extractable fraction increased significantly from 1.3 to 4.9 mg/kg, which represents 2.1 and 7.1% of the total content, respectively. In soil, Zn in mainly bound as oxide (10.0%) and in the residual fraction (80%). From the sequential analysis, the percentage of the oxide bound fraction increased up to 16% in treated soils and the zinc fraction linked to organic matter increased in treated soils from 1.2% to 2.1%. The residual zinc fraction decreased. There is a significant linear correlation between the DTPA-extractable fraction and the Zn fraction linked to the organic matter ($r^2 = 0.68$) and the oxide fraction ($r^2 = 0.69$).

Sample Point	**Silt (%)**	**Clay (%)**	**Sand (%)**	**pH**	**O.M. (%)**	**EC$_{(1:5\ water\ extract)}$ dS m-1**	**CaCO$_3$ (%)**
1	42	10	48	8.6	0.47	0.17	37.8
2	40	12	48	8.4	0.10	0.17	38.7
3	45	12	43	8.6	0.59	0.19	38.7
4	41	8	51	8.3	0.31	0.19	20.3

Table 1: *Soil characteristics of the 0-20 cm surface soil for the four positions along the vineyard slope*

Discussion and conclusions

The data show an increase of total metal content in the soil after compost application. The type of metal speciation is similar in treated and in untreated soils. Cu is mainly in the organic matter fraction and Zn is bound to oxides. The percentage of these fractions increased after compost application, and the residual fraction decreased.

The DTPA-extractable fraction, which is equivalent to the metal fraction taken up by plants, also increased after compost application. This fraction corresponds with the organic matter fraction for Cu and with the organic matter and oxides fractions for Zn. Metal distribution depends on the element, and soil properties such as pH and soil moisture conditions (Han *et al.*, 2001). These authors noted that in arid soils the reducible oxide fraction and the organically-bound fraction increases after addition of compost, although the carbonate fraction is the most abundant in the soils they analysed.

In this study, the high pH favours the fixation of these elements to soil. The movement of these elements in soil is of concern due to potential impacts on the environment through surface water by runoff. There are a few examples in the literature of increased concentrations of metals in surface waters resulting from spreading organic wastes on farmland (Boy and Ramos, in press; Farsang *et al.*, 2005).

Therefore, metals applied to soil with compost or other wastes contribute not only to an increase in the total metal content of the soil, but also to an increase in the amount of metals that can be utilized by crops or can leach into the environment. This represents a potential hazard for the development of sustainable agriculture practice.

Soil sample	**Cu (mg kg^{-1})**		**Zn (mg kg^{-1})**	
	Total Cu	DTPA-Cu	Total Zn	DTPA-Zn
P1	38.2	7.48	54	0.82
P1(+)	41.7	9.1*	60.8*	4.72*
P2	34.0	3.2	59.70	0.96
P2(+)	43.9	6.6*	73.7*	3.6*
P3	33.2	5.5	57.80	2.2
P3(+)	43.9	7.3*	65.9*	5.38*
P4	42.7	6.9	65.0	1.16
P4(+)	44.9	9.5*	77.9*	6*
Average				
Pi	37.0±4.0	5.8±1.9	59 ± 4	1.3±0.6
Pi(+)	43.6±1.4	8.1±1.4	69 ± 10*	4.9±1.0

(* significant differences between treated and untreated soils, p<0.05)

Table 2: *Total metal content and the DTPA-extractable fraction for treated (Pi(+)) and untreated soils (Pi)*

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Meeting report

World Wetland Day Conference 2005

Wetlands: Focus on Delivery

The World Wetland Day (WWD) Conference 2005 (Wetlands: Focus on Delivery), attended by over 150 delegates, was held at the School of Oriental and African Studies (SOAS), London, on 31st January and 1st February, 2005. This fourth UK WWD conference was organised by Coastal Management for Sustainability (CMS) on behalf of the Chartered Institution of Water and Environmental Management (CIWEM). The aims of the conference were to bring together key organisations in the UK involved in managing wetlands, and to promote the many uses and the biodiversity of wetlands.

The first day was based at the London Wetland Centre (LWC) with walks led by Wildfowl and Wetlands Trust (WWT) staff and a discussion on “creating and managing wetlands for wildlife and people”. The 40 hectare LWC is a purpose built wetland environment built on the site of four redundant Victorian reservoirs in Barnes, London. The project was a collaboration between the WWT, the local London Borough Council and a property development company. Following its opening in May 2000, the Centre has attracted resident and migratory wildfowl, including Gadwall and Shoveler ducks, and has been designated a Site of Special Scientific Interest (SSSI).

London Wetland Centre

In the evening, a wine reception was followed by a curiously poetic keynote presentation from Professor Brian Moss, Liverpool University, entitled “Wetlands, wolves and the courtship of hippopotami”. His talk focussed on the dependence and interdependence of all living things on water, and he discussed the deterioration of wetlands in the UK and abroad, the Water Framework Directive (WFD), and different wetland management techniques.

The second day of the conference was held at SOAS and consisted of a series of workshops on wetland management. Underpinning the discussions was the recent introduction of the WFD 2000/60/EC, and there were agricultural, environmental, and recreational perspectives on managing and conserving UK wetlands, with speakers from the RSPB, WWT, Environment Agency, English Nature, English Heritage, local authorities, and environmental consultancies.

Weblinks

London Wetland Centre http://www.wwt.org.uk/visit/wetlandcentre/

Royal Society for Protection of Birds (RSPB) http://www.rspb.org.uk/

Water Framework Directive http://www.defra.gov.uk/environment/water/wfd/

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Meeting report

The 2005 Environmental Chemistry Group Distinguished Guest Lecture and Symposium

The 2005 ECG Distinguished Guest Lecture and accompanying Symposium were held in the Council Room of the Royal Society of Chemistry, Burlington House on March 2nd. The theme for this well-attended meeting was “Metals in the environment: estimation, health impacts and toxicology.”

Dr Jörg Feldmann, from the Trace Element Speciation Laboratory Aberdeen, University of Aberdeen, opened the meeting with a review of arsenic metabolism. Dr Feldmann described the speciation of arsenic* and how the toxic effects of arsenic were related to its speciation. Although the acute toxicity of arsenic is well known, in recent years the effects of chronic toxicity linked to exposures to low concentrations of arsenic species have become more apparent. More than 70 million people worldwide are exposed to arsenic, and health effects such as hyperkeratosis and skin and bladder cancer have been observed in some regions. The precise mechanisms of arsenic toxicity are as yet unknown. Dr Feldmann contrasted arsenobetaine, which is present in fish and shellfish, but is not metabolised when ingested and is excreted unchanged in urine with no acute toxicity and no chronic effects, with arsenic III/V, which is present in water and vegetables, has a high acute toxicity, severe chronic effects, accumulates in hair, nails and skin, and is metabolised to DMA(III) & DMA(V) and MMA(III) & MMA(V) before excretion.

Identification of the arsenic species is particularly important when assessments of toxicity are made, and any analytical procedures need to have good speciation specificity. The range of arsenic metabolites (*e.g.* glutathione complexes, phytochelatins) demands access to a variety of species-discriminatory analytical methods. Dr Feldmann discussed the use of HPLC-ICP-MS and HPLC-ES(electrospray)-MS for the determination of arsenic species (with detection limits of around 1ng mL^{-1}), and the application of XAS (X-ray Absorption Spectroscopy) and XANES (X-ray Absorption Near Edge Spectroscopy) for *in situ* speciation of arsenic. These techniques were used to investigate the metabolism of arsenic sugar species in seaweed eaten by sheep in the Orkneys. Dr Feldmann commented that the identification and quantitative analysis of the wide range of arsenic-sulphur species that exists in biological systems will open a new chapter in arsenic speciation.

In the second presentation of the afternoon, **Dr Andrew Smith** (MRC Toxicology Unit, University of Leicester) spoke on “Toxicogenomic approaches to determine consequences of metal exposure”. The traditional concerns of toxicologists in relation to drug responses and occupational exposures have been replaced by interests in carcinogenicity and neurotoxicity. In particular, the identification of neuronal effects and their influence on development were especially important for metals such as Mn, Fe, Ni, As, Pb, Hg and Cd where low concentrations produced low levels of neurotoxicity. For such effects the embryo and the very young were at greatest risk. Although mechanistic studies of such impacts had great intrinsic value, he pointed out that even if the identification of exact mechanisms of toxicity helped our understanding of the hazards of exposure to particular species, such investigations did not always assist in the quantification of risk.

New methodologies, including toxicogenomics, proteomics, and metabonomics (see *ECG Bulletin*, July 2004), provide new testing protocols for the toxicologist. These methods have an immense range of possibilities, but also produce large amounts of data with as yet no unified method of presentation. Examining how gene transcription, the nature and quantity of proteins, or the expression of metabolites varied after a toxicological insult might give an indication of occupational or environmental exposure. But the influence of variables such as diet (nutritional status), polymorphisms (individual genetic type) confounded the interpretation of results from such work. Dr Smith thought that metabolite expression might be the way ahead to link exposure to toxicity and gene function.

The closing session celebrated the work of **Professor Jane Plant** CBE (currently at Imperial College and ex-Chief Scientist at the British Geological Survey (BGS)). Her presentation was entitled “Chemicals in the Environment”. Professor Plant began by exploring the manner in which the evolution of man was linked to the increasingly sophisticated use of chemicals. This usage was changing with the introduction of new technologies that involve new modes of transport, communications, nanotechnology and similar. As man’s use of chemicals changes (and increases) so does the risk of health effects increase. Although many of the chemicals that are in the environment naturally or as a consequence of man’s activities are essential for life, the effects of metal deficiencies are apparent only at very low concentrations and exposure to a small excess of an essential element can easily produce chronic toxicity.

Professor Plant explored the way in which high resolution mapping of multi-element distributions in the UK could assist in estimates of metal bio-availability and subsequent health risks. She went on to argue that in the long term only the sustainable use of chemical resources could resolve the issues associated with the increasing redistribution of geologically ‘fixed’ chemicals by anthropogenic activity, and that the best way to address such sustainability issues was *via* Life Cycle Analysis (LCA).

The interlinking of toxicity studies (speciation, analysis, mechanisms, risk) with mapping of chemicals (spatial distribution, risk assessment) and efforts to mitigate hazards and risk (sustainable use, LCA) needs to be internationally targeted and prioritised.

The symposium ended with a series of questions, some of which reflected the concern of the delegates about the significant costs involved in accessing the BGS mapping data and the detrimental impact this has on education and research.

More detailed accounts of the three presentations from the ECG DGL 2005 will appear in the January 2006 issue of the *ECG Bulletin*.

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*Examples of arsenic speciation

Name	Abbreviation (Alternative Abbreviation[†])	Chemical formula
Arsenite, Arsenous acid	As(III)	$As(OH)_3$
Arsenate, Arsenic acid	As(V)	$AsO(OH)_3$
Monomethylarsonic acid	MMA(V) (MA)	$CH_3AsO(OH)_2$
Monomethylarsonous acid	MMA(III) [MA(III)]	$CH_3As(OH)_2$
Dimethylarsinic acid	DMA(V) (DMA)	$(CH_3)_2AsO(OH)$
Dimethylarsinous acid	DMA(III)	$(CH_3)_2AsOH$
Trimethylarsine oxide	TMAO	$(CH_3)_3AsO$
Trimethylarsine	TMA(III)	$(CH_3)_3As$
Arsenobetaine	AsB (AB)	$(CH_3)_3As^+CH_2COO^-$
Arsenocholine	AsC (AC)	$(CH_3)_3As^+CH_2CH_2OH$
Tetramethylarsonium ion	Me_4As^+	$(CH_3)_4As^+$
Dimethylarsinoylethanol	DMAE	$(CH_3)_2AsOCH_2CH_2OH$
Arsenosugars	X, XI, XII, XIII, XIV, XV	

[†] Abbreviations for arsenic metabolites have not been standardised. See ‘Determination of arsenic species: A critical review of methods and applications, 2000–2003’, Kevin A. Francesconi, Doris Kuehnelt, *Analyst*, 2004, (5), 373-395.

Meeting report

Faraday Discussion 130: Atmospheric Chemistry

Two-hundred delegates attended Faraday Discussion 130 on *Atmospheric Chemistry* at the University of Leeds held on 11-13 April 2005.

The opening session of the meeting was concerned with modelling chemistry-climate interactions and the impacts of climate change (Pyle, Cambridge; Stevenson, Edinburgh). In a plenary lecture, “Chemistry-climate coupling: the importance of chemistry in climate issues”, Ravishankara (NOAA, Boulder) posed the questions “How does the chemical composition of the atmosphere influence climate and how does climate affect chemical composition?” Several issues arose from the papers by Pyle and Stevenson, and a need was expressed for a greater understanding of:

- How stratospheric–tropospheric ozone exchange is affected by climate change;
- How the behaviour of ozone in the Lower Stratosphere and Upper Troposphere correlates with El Nino;
- How climate change induced humidity increases might influence ozone concentrations (*via* $O(^1D) + H_2O \rightarrow 2OH$);
- The effects of convection and circulation on tropospheric ozone concentrations;
- The effects of temperature on tropospheric ozone (for example *via* increased isoprene emissions from tropical forests).

Photochemistry and reaction kinetics of small molecules were the topics for the second session. Such data are important for chemical and dynamical simulations of atmospheric chemistry, which increasingly require more accurate mechanisms, rate constants and Arrhenius parameters. Seakins (Leeds) reviewed kinetic data on the photolysis of methyl ethyl ketone, diethyl ketone, and methyl vinyl ketone. These compounds are formed from the oxidation of hydrocarbons and are also produced in significant amounts biologically. They have long atmospheric lifetimes and make a significant contribution to the HO_x budget. Ingham (Leeds) presented the results from a study of ClOOCl reactions with Br, Cl and NO, which was undertaken with Sander and Friedl from the California Institute of Technology. Current models over-predict ClOOCl by 30% and new studies of ClOOCl absorption cross sections may be necessary. The final paper in this session (Hynes and co-workers, Miami) was a kinetic and mechanistic study of the recombination of OH with NO_2.

In the opening lecture on the second day of the meeting, Platt and co-workers (Heidelberg) discussed the value of Multi Axis Differential Optical Absorption Spectroscopy (MAX-DOAS) for analysing gas and aerosol distributions. This technique uses a set of slant column density measurements obtained with the sun as an ‘analytical light source’ to measure scattered light from several different elevation angles. From the data, a simple algorithm can be applied to determine the atmospheric aerosol extinction and the absolute concentration and mixing ratio of NO_2 within the atmospheric boundary layer. The apparatus seemed relatively simple (miniature spectrometer, a small telescope, a pointing mechanism and a PC) and offers an opportunity to track NO_2 plumes at ground level which may well be useful for statutory air monitoring purposes.

Monks (Leicester) described plume monitoring in the Leicester area. Jones (Cambridge) explained that the simplified night-time chemistry of NO_x is an opportunity to examine the small scale structure of the chemistry which occurs in plumes. His work clearly showed the non-linear, non-homogenous distribution of the chemistry in a plume, and his conclusion that one “cannot neglect the near source structure and mixing in local and regional NO_x and O_3 budgets” may have implications for National Air Quality Strategy monitoring protocols. Tuck (NOAA) talked about small scale variation in atmospheric chemistry under conditions when Maxwell-Boltzmann conditions did not apply, *i.e.* when there was a long tail of high velocity molecules. He argued that research into such phenomena was essential for an understanding of how tropospheric warming effected stratospheric cooling, and he used the large fluctuations in tropospheric methane concentrations on a small temporal and spatial scale as an example.

In the second morning session, George (Laboratoire d’Application de la Chimie a l’Environnement) discussed the photoenhanced uptake of NO_2 onto solid organic compounds to give HONO (an important source of OH), and this was followed by a paper (Abbatt, Toronto) which examined the uptake of gas phase nitric acid onto ice with evidence for unsaturated surface coverage at low partial pressures. The interactions of nitric acid, VOCs, $ClONO_2$ *etc.* on cirrus clouds were linked into the formation of OH *via* HONO chemistry. Donaldson (Toronto) gave a paper on the uptake and reaction of atmospheric organic vapours on organic films. This topic is relevant to oxidation reactions that occur on 'urban surfaces'.

Secondary organic aerosols (SOA) was the subject for the afternoon sessions. Baltensperger (Paul Scherrer Institut, Switzerland) examined the dependence of SOA growth rates on organic compound oligomerisation processes using α-pinene and trimethylbenzene in experimental systems. Herrmann (Leibniz Institut) discussed SOA formation from terpenes, and indicated that SOA yields depended on temperature, seed nuclei type, monomer molecular mass and monomer volatility. Using experimental and computational techniques, Donahue (Carnegie Mellon) examined the critical factors which determine the variation in SOA yields from terpene ozonolysis. The final session of the second day focused on NMVOC (non-methyl volatile organic compounds) and their impact on oxidant and aerosol formation (Jenkin, Imperial College). Kolb (Aerodyne Research) described mobile ground level monitoring and the way in which it (as opposed to sparse fixed site air quality monitoring stations) could deal with the variable (temporal and spatial) emission sources which produce small area chemical gradients at ground level. McFiggans (Manchester) described the use of a Master Chemical Mechanism which was a simplified representation of the organic component of atmospheric particulates.

Burrows (Bremen), in the opening session on the final day, reviewed the remote sensing of atmospheric composition from space and gave a clear exposition of the difficulties and approximations involved. Jaegle (Washington) followed with a paper which illustrated how satellite observations could be used to examine the relative roles of fossil fuel combustion, biomass burning and soil emissions as NO_x sources. There is a surprisingly large contribution (22%) from soil emissions to global surface NO_x emissions. Bloss (Leeds) examined the way in which the various measurements of the oxidative capacity of the troposphere (OH concentrations) could be reconciled. The final session examined the hydrophilicity of atmospheric particles (Seisel, Essen), calcium carbonate dust particles (Rudich, Weizmann) and a study of the products, mechanisms and kinetics of reactions between ozone and oleic acid particles (Ziemann, Riverside).

The proceedings from Faraday Discussion 130 will be published by the Royal Society of Chemistry in late 2005.

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Royal Society of Chemistry Analytical Division

Atomic Spectroscopy Group

Hilger Prize

Nominations for the 2006 Hilger Spectroscopy prize are invited. The award is judged on the basis of the candidate's contribution to analytical atomic spectroscopy, which may be in such fields as atomic absorption, atomic fluorescence, atomic emission, ICP-MS and X-ray fluorescence spectroscopy. The contribution need not be theoretical and may include areas such as applications, instrumental development or modification, improvement in data handling, calibration procedures or sample preparation.

The prize is open to **anyone under the age of 35 on December 31st 2006** who is a member of the **Analytical Division of the RSC and whose work involves the use of atomic spectroscopy**. The applicants will be required to submit a short summary of their work (2 pages maximum), together with a brief CV and a list of their publications by **31st March 2006**.

The winner will receive a cash/book prize and additionally an opportunity to present their work at the 13th Biennial National Atomic Spectroscopy Symposium which will be held at the Glasgow Caledonian University from the 10th to 12th July, 2006. Free registration will be provided to help attend this major conference on atomic spectroscopy.

APPLICATIONS SHOULD BE SENT, PREFERABLY IN ELECTRONIC FORM, BY 31st MARCH 2006, to the Honorary Secretary of the Atomic Spectroscopy Group, Dr. A. Fisher, School of Earth, Ocean and Environmental Sciences, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA. e-mail: AFisher@plymouth.ac.uk

Forthcoming meeting
Impacts of climate change on air quality

The 2006 Environmental Chemistry Group Distinguished Guest Lecture and Symposium

London, March 2006

'Clear science demands prompt action on climate change say G8 science academies'

In a united attempt to alert political leaders to the existence and consequences of climate change, the G8 Science Academies issued a joint statement on June 7th 2005. The statement calls on the G8 nations to: "Identify cost-effective steps that can be taken now to contribute to substantial and long-term reductions in net global greenhouse gas emissions." And to, "recognise that delayed action will increase the risk of adverse environmental effects and will likely incur a greater cost." The **2006 ECG DGL and Symposium** will examine one aspect of the consequences of climate change - the impacts of climate change on air quality. The 2006 Distinguished Guest Lecturer will be **Professor Mike Pilling** from the University of Leeds. Further details of this event will be given in the next issue of the *ECG Bulletin.*

Weblink: Joint Science Academies' statement: 'Global response to climate change' http://www.royalsoc.ac.uk/displaypagedoc.asp?id=13057

Meeting report

9th Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research

University of Leicester, 20-21 April 2005

Over the past nine years, UK air pollution research groups have participated in annual meetings hosted by the MRC Institute for Environment and Health (IEH), Leicester. This year's meeting was attended by 70 delegates with 22 speakers and 14 poster presentations. Some highlights are summarised below. The full proceedings of the 9th Annual UK Review Meeting on Outdoor and Indoor Air Pollution Research are available at http://www.le.ac.uk/ieh/pdf/W22.pdf

Session 1: Atmospheric chemistry, exposure measurement and modelling

The first session was opened by Monica Price (Sunderland), who made a 'Comparison of black smoke and PM_{10} measurements from co-located monitors at three UK sites'. Price argued black smoke (BS) to be a better indicator of health effects than particulate matter (PM). On a related theme, Fu-Meng Khaw (Newcastle upon Tyne) presented a study into the relationship between historical SO_2 levels and black smoke exposure in North East England. The study found SO_2 could be used as a predictor for BS, and will be used as part of a larger project to estimate long-term exposure to air pollutants in a cohort of 1142 babies born in Newcastle upon Tyne, in May and June 1947 – the Newcastle Thousand Families Cohort.

Abhishek Tiwary described the University of Nottingham's research into hedgerow effects on aerosol filtration and dispersion. The work has applications for mitigating pesticide drift from farmland to residential properties. Porous hedges such as the Holly bush proved to be more efficient at filtering particles from air than the denser hedgerows such as Yew.

Session 2: Exposure measurement and modelling (1)

Sirinath Jamieson (Imperial College, London) began the second session with a presentation on 'Exposure measurements of indoor ultra fine particles: a pilot study on the night-time patterns'. Elevated ultrafine particle concentrations were observed during indoor activities such as cooking and vacuum cleaning, but the particulate level decreased during zero activity (sleep). Still indoors, Ivan Gee (Manchester) highlighted that carpets in houses with inhabitants who smoke were a source of endotoxins.

Alex Ledbrooke (Cornwall College) reviewed the 'Cornwall Air Quality Strategy: air quality issues in an isolated rural area'. A poor road infrastructure was of particular concern for its effect on localised air quality.

Session 3: Exposure measurement and modelling (2)

The exposure measurement and modelling session continued with Alison Tomlin (Leeds) who talked about 'Factors influencing exposure to traffic related pollutants in urban streets'. By monitoring traffic characteristics, correlations were found between CO_2 and vehicle occupancy. The results showed congestion to be a bigger contributing factor to elevated pollution concentrations than vehicle numbers. Tomlin also presented models of pollution in streets, and described the effects of topography, wind direction and traffic emissions.

Susan Hodgson (Imperial College, London) and Richard Mohan (Chemical Hazard and Poisons Division, London) both described dispersion modelling around a point source: a Chlor alkali plant in Runcorn and a landfill site respectively.

Session 3: Ultrafine seminar (1)

Roy Harrison (Birmingham): 'Formation and dispersion of ultrafine particles: composition, lifetime, monitoring and modelling'. Anthony Seaton (Institute of Occupational Medicine, Edinburgh), 'The ultrafine hypothesis after ten years'.

Session 4: Ultrafine seminar (2)

Ken Donaldson (Edinburgh): 'Reactions of ultra fine particles and biological systems'. Martin Meadows (DEFRA): 'Policy implications'.

Session 5: Mechanisms

Martin Wilson (Napier University, Edinburgh): 'Nanoparticle and metal interactions and their impact on lung toxicology'. Michael Routledge Leeds): 'DNA damage and mutations induced by urban particulate matter'. Sarah Kemp (Imperial College, London): 'Effects of nanoparticles on mediator release by primary human alveolar epithelial cells and macrophages'.

Session 6 : Epidemiology and human health (1)

Hazel Jones (Imperial College London) discussed the use of Position Emissions Tomography (PET) to assess the effects of smoking on the lungs. This non-invasive technique allowed repeated examination of the lung tissue, which revealed that 'inflammatory cell activity in the lungs of smokers is modulated even by a relatively modest acute insult'. Richard Atkinson (St Georges' Hospital Medical School, London) of the APHENA (Air Pollution and Health: a Combined European and North American Approach) project presented the 'results of analyses of hospital admissions'. The work highlighted a need for sensitivity analysis in studies of the short-term health effects of particles and ozone on respiratory hospital admissions. Ben Barrett (King's College, London) then talked about the proposed investigation into the health impacts of the London Congestion Charging Scheme. This is to be a three-year study starting in 2005.

Session 7: Epidemiology and human health (2)

Stephen Bremner presented results of a study linking hospital admissions and particle species. This involved logging admissions, age, sex, diagnosis *etc.* with information downloaded daily from the internet. The results were inconclusive, although sulphate and ozone were deemed to be associated with an increased risk of admissions across the broad range of diagnostic and age sub groups.

Christina Yap reported an investigation into long term exposure to air pollution in Scotland. The study has lasted for 22 years and has involved 22,000 subjects in an area where detailed records of black smoke exist. The research found 'convincing evidence' of a link between exposure and cancer. There were, however, missing data, and variables such as house and traffic density were not taken into consideration. This information will be added to the research, which will be reassessed to clarify the findings.

The final presentation of the conference was by Roseanne McNamee (Manchester) who described an investigation into whether or not 'cardiopulmonary patients are more susceptible to pollutant-related mortality'.

A. LEDBROOKE, Air Quality Unit, Cornwall College

Comment: Fish stocks, endocrine disruptors, and global warming

Following an article on endocrine disruptors in the previous issue of the *ECG Bulletin*, **Alan Wiseman** comments on other environmental threats to fish stocks.

The laudable article in the January 2005 issue of the *Environmental Chemistry Group Bulletin* (pp 4-6) by E. M. Hill and C. M. Tyler, "Endocrine disruption and UK river fish stocks", emphasised the accumulation in the bile of oestrogens and mimics (10^4 – 10^5 fold). Using the YES bioassay (recombinant yeast containing oestrogen receptor) with reverse phase HPLC/MS techniques, a range of oestrogens were identified in the immature rainbow trout.

Nevertheless, especially where stocks of the gudgeon (*Gobio gobio*) are threatened by endocrine disruptors, other factors may determine the survival outcome! These factors include the effects of water temperature on dissolved oxygen concentration (DOC). DOC is lower at higher temperatures, and biological oxygen demand (BOD) of the effluent waters will modulate the outcome (Lynch and Wiseman, 1998).

Furthermore, global warming, somewhere in the wide range of 2 – 11 °C in this century, has been predicted by a variety of models set up in computers worldwide (Stainforth, Alna, Christensen, Collins, Faull *et al.* 2005). Moreover, survival chances of individual species of fish, such as the river trout, should be extrapolated now to accommodate the ongoing global warming (from an anthropogenic cause or otherwise) associated with the rising atmospheric level of greenhouse gases, such as carbon dioxide and methane. In addition, presently pertinent data will be replaced very soon by updated findings of further investigations of the pollution caused by endocrine disruptors such as oestrogens and mimics.

References

Lynch, J.M. and Wiseman, A. (eds.), *Environmental Biomonitoring: The Biotechnology Ecotoxicology Interface*, Cambridge University Press, Cambridge, 1998.

Stainforth, D.A., Alna, T., Christensen, C., Collins, M., Faull, N., *et al.* Uncertainty in predictions of climate response to rising levels of greenhouse gases. *Nature*, 2005, **433**, 403-406.

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. . . Elizabeth Hill replies:

There are numerous stresses affecting fish population in UK rivers, and endocrine disrupting chemicals are one of them. The finding that intersex fish in effluent-contaminated waters have reduced fertility suggests the possibility of deleterious population changes in a number of UK fish species (Jobling *et al.*, *Biology of Reproduction*, 2002, **67**, 515-524). In addition, the impact of climate change, resulting in less dilution of effluents (some of which are barely diluted in receiving waters in summer) are likely to exacerbate this type of pollution unless additional wastewater treatment technologies are deployed.

Wiseman makes an important point that depletion of oxygen levels in rivers due to climate change and BOD may also affect survival of sensitive fish species. In addition, the reports that sub-lethal levels of hypoxia can also impair fish reproduction and embryonic development raises further concern on the future health of fish populations in rivers (Wu *et al.*, *Environmental Science and Technology*, 2003, **37**, 1137-1141; Shang and Wu, *Environmental Science and Technology*, 2004, **38**, 4763-4767). These stresses combined with inputs of an array of effluent-associated xenobiotics – including some pharmaceuticals, the loss of habitat diversity, and the effects of damming (weirs) – which inhibit fish movement, all suggest that river environments are still amongst the most vulnerable ecosystems in the world with regard to anthropogenic impacts.

E. M. HILL,
University of Sussex,
June 2005

Meeting report

Pharmaceuticals in the Environment

Organised by the SCI BioActive Sciences group in association with JPAG, RSC and SETAC-UK, this meeting was held in March 2005 at the Society of Chemical Industry, Belgrave Square, with an attendance of about 120.

The topic for the meeting was introduced by **Mark Cronin**, (Liverpool John Moores University), who noted that although there are data on the presence and distributions of some pharmaceuticals in the environment, relatively little is known of their biological effects on ecosystems.

Emma Pemberton (Environment Agency) explained how the types of pharmaceuticals that do enter the environment are related to their overall usage. Among the 5,500 active pharmaceutical ingredients approved for human use, the top 50 pharmaceuticals by usage include paracetamol, lactulose, ibuprofen, acetylsalicylic acid, and amoxycillin, which are all used at levels of around 100 tonnes/annum. The next level includes ranitidine, cimetidine, carbamazepine, and erythromycin which are used at levels of between 10-100 tonnes/annum. By contrast, only about 450 veterinary medicines are authorised. Usage of antimicrobial medicines is around 450 tonnes/annum (*ca.* 50% of which is accounted for by tetracycline), organophosphorus sheep dip (50.2 tonnes/annum), coccidiostats (214 tonnes/annum) and growth promoters (13 tonnes/annum).

For human pharmaceuticals, the primary route into the environment is through sewage treatment plants – the combined effect of excretion and improper disposal of unwanted drugs. Most sewage treatment works are likely to discharge low levels of pharmaceuticals, and in several cases measurable amounts are present in the receiving waters. In a UK study, twelve compounds were monitored in sewage works at low flow conditions. Ibuprofen levels were very much greater in effluent and in receiving waters than other compounds, reflecting a low level of metabolism and relative persistence. Seven other pharmaceuticals were also found. The study concluded that most sewage works release pharmaceuticals in measurable amounts, with variations in individual sewage treatment works.

Alex Tait (Veterinary Medicines Directorate) outlined European Union environmental legislation for human and veterinary pharmaceutical products, which are covered by Directives 2001/83/EC (amended 2004/27/EC) and 2001/82/EC (amended 2004/28/EC), respectively. Some veterinary medicines have been refused Marketing Authorisation on the basis of environmental safety whereas many human medicines have been approved without an environmental assessment due to the absence, at present, of appropriate guidelines.

Len Levy (MRC Institute for Environment and Health, University of Leicester) reviewed the indirect effects of veterinary medicines on consumers. The main concerns are the long-term fate of these products in the environment and risks to health, which result from indirect exposure. Around 90 compounds were selected for their potential impact on human health using a priority scheme. Of these, 31 compounds were identified as being of particular concern. The range of compounds was expanded to 48 to include some that are not licensed for veterinary use but which find their way into the environment. Low or no effect levels for significant endpoints (*e.g.* neurological, developmental, mutagenic and carcinogenic effects) were estimated using literature data relevant to low-level, long-term exposure. The overall aim is to assess the likely exposure of humans to the priority veterinary medicines. Combining the exposure data with hazard information will allow assessment of risk. Refinements to the model will include additive effects of compounds with similar health effects and consideration of sensitive subgroups in the population.

Kevin Thomas (CEFAS) gave a talk on the occurrence of human pharmaceuticals in the UK aquatic environment. Measurements (HPLC-ESI MS) were carried out in wastewater works, rivers and estuaries for the 500 most used pharmaceuticals. Of the five sewage works monitored, ten of the targeted pharmaceuticals were identified. Ibuprofen had the highest measured environmental concentration (MEC) at *ca.*3 mg L^{-1}. Upstream samples were clean whereas discharge and downstream samples showed similar relative abundances. Eight of the targeted compounds were identified in receiving waters, with ibuprofen again at the highest MEC (1 mg L^{-1}). Analysis of six stations along the Tyne estuary revealed the presence of nine of the targeted compounds and showed that Howden water treatment works accounts for 80% of the effluent that goes into the Tyne.

Katherine Fenner (EAWAG, Switzerland) outlined the challenges in exposure modelling for pharmaceuticals. The main focus of modelling studies for pharmaceuticals in the environment is the transfer from soil/sediment/sludge to groundwater. There is little guidance on how to estimate elimination from sewage treatment plants and there is little detailed knowledge of the pathways of breakdown. The main uncertainty in exposure modelling is in the treatment of pharmaceutical release and transport into water systems from sludge or manure that has been applied to soils.

Most exposure models assume that sorption is dominated by adsorption to organic matter. However, pharmaceuticals associated with sludge and soil show little correlation between log K_{oc} and log K_{ow}, indicating that organic carbon content is not a good descriptor to model sorption. Thus, sorption is dominated by polar and charged interactions associated with the polar nature of the pharmaceuticals.

Liz Wellington (University of Warwick) discussed the impacts of clinical and non-clinical usage of antibiotics and biocides on environmental reservoirs and mobility of resistance genes. Bioavailability of pharmaceuticals in the environment has the potential to affect natural microbial populations through the development of resistance genes. The prevalence of microbial resistance to pharmaceuticals indicates that delivery of compounds *via* manure and industrial effluent impacts on resistance gene reservoirs. The prevalence and spread within indigenous bacteria suggests the involvement of plasmids. The differences in resistance quotients between natural soil bacteria and bacteria in chicken litter are vast, indicating active development in antibiotic augmented situations.

Two sites, an arable field deliberately polluted with antibiotics and a heavily polluted effluent treatment reed bed at a textiles works, were examined for the spread of antibiotic resistance. Pig slurry from tylosin-fed pigs was amended with sulfachloropyridazine and oxytetracycline before being spread on the arable field. Around 65% of bacterial isolates contained a known sulphonamide resistance gene. Examination of bacterial isolates revealed a range of soil bacteria with a mobile R plasmid. Further work confirmed the transfer of genes to soil bacteria *via* plasmids and integrons. Only isolates from the reed bed itself showed the presence of a class 1 integron that was disseminated widely among the aquatic bacteria. (Integrons are mobile DNA elements with the ability to capture genes, notably those encoding antibiotic resistance, by site-specific recombination).

The presence of *qacE* genes and antibiotic resistance genes indicates that pollution from quaternary ammonium compounds such as detergents and surfactants increases selection pressure and facilitates the spread and persistence of antibiotic resistance among natural bacterial populations.

In a talk on ecotoxicity tests for pharmaceuticals, **Tim Williams** (AstraZeneca) suggested that the focus should be on the long-term environmental effects of pharmaceuticals. Evaluation of impacts based on acute data is not appropriate. The base data set is the Phase II Tier A data involving ecotoxicological testing for algal growth inhibition (Organisation for Economic Co-operation and Development; OECD 201), *Daphnia* reproduction test (OECD 211) and fish early life-stage test (OECD 210). For Phase II Tier B assessment, log K_{ow} values ≥ 4 are used as a criterion for bioaccumulation and indicate a requirement for the analysis of terrestrial effects. Given that the timescales involved in order to achieve regulatory compliance can be long, it is necessary to include the testing during the drug development phase.

Early screening of candidate drugs can be performed prior to seeking regulatory compliance. This necessitates the selection of appropriate tools for the assessment, good speed and efficiency, and predictions of potential long-term effects. The real question is "can we account for ecotoxicology in drug design?" Accordingly, the current direction of research is to:

- Understand the mode of action and mechanisms of effect;
- Determine differences between different classes of organism;
- Make better use of mammalian data to predict ecological responses, and
- Use "direct" testing strategies.

For example, the impact of tamoxifen citrate on life cycle of fathead minnow (*Pimephales promelas*) has been examined. The life cycle and size of the fathead minnow is such that it is possible to test to maturity in about one year, and various different growth stages and indicators are examined. In particular, the presence of the female sex hormone vitellogenin in male fish is used as a mechanistic signpost for estrogen disruptors and can contribute to overall body of evidence required to identify a significant impact.

Alistair Boxall (University of York/ Central Science Laboratory) concluded the scientific programme with a talk on the fate of pharmaceuticals in the environment. Pharmaceuticals enter the wider environment through a variety of routes including biosolids (sludge, slurry, direct excreta) and irrigation. A key consideration is their fate with respect to release into soils. Detailed studies have been carried out with three antibacterial compounds representative of sulfonamide, tetracycline and macrolide antibiotics, respectively.

Sulfachloropyridazine had a low sorption coefficient (K_d) in soil and soil/slurry, indicating it to be highly mobile. Oxytetracycline had a high K_d and hence was moderately persistent. Tylosin was not detected in any of the soil samples. The nature of the matrix was also shown to be important. Thus, in sandy soil sulfachloropyridazine was found to have a half-life of about 6 days, indicating a lower potential to leach to groundwater. A marked pH dependence of K_d was noted for oxytetracycline. The macrolide tylosin exhibited a half-life of less than 2 days in slurry but was persistent in soils, having sorption characteristics intermediate between sulfachloropyridazine and oxytetracycline. In general, metabolites were found to be less sorptive than the parent compounds.

The test compounds were applied to the test soils in pig slurry, and leachate was monitored over a period of four months. At the end of that time the soil was also analysed. Only sulfachloropyridazine was observed in the soil or the water, indicating that oxytetracycline and tylosin will not leach to groundwater following slurry application. The affinity of sulfachloropyridazine for the aqueous phase is important to its mobility. Although antibiotics are released to soils and have the potential to persist for some time, their transport to surface waters and groundwater is variable and where this did occur, the environmental concentrations were lower than the effect concentrations.

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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 January to May 2005.

Asphalt (Bitumen)
(Concise International Chemical Assessment Document No. 59)

World Health Organization, Geneva, 2004, ISBN/ISSN: 9241530596

Chemical Science Priorities for Sustainable Energy Solutions

Royal Society of Chemistry, Cambridge, 2005

Chloroform
(Concise International Chemical Assessment Document No. 58)

World Health Organization, Geneva, 2004, ISBN/ISSN: 9241530588

1-Chloro-1,2,2,2-Tetrafluoroethane (HCFC 124), 2nd edition
(ECETOC Joint Assessment of Commodity Chemicals (JACC) No. 46)

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 2004, ISBN/ISSN: 0773633946

Glyoxal
(Concise International Chemical Assessment Document No. 57)

World Health Organization, Geneva, 2004, ISBN/ISSN: 924153057X

IARC Monographs on the Evaluation of Carcinogenic Risks to Humans
(IARC Monographs Vol. 84)

World Health Organization, Geneva, 2004, ISBN/ISSN: 9283212843

Introduction to Environmental Analysis

R. Reeve, J. Wiley, Chichester, 2002, ISBN/ISSN: 0471492957

Local Authority Health and Safety Enforcement

C. N. Penn, Shaw & Sons Ltd., Crayford, 2005, ISBN/ISSN: 0721916503

Soil and Sediment Risk Assessment of Organic Chemicals
(ECETOC Technical Report No. 92)

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 2004, ISBN/ISSN: 0773807292

Targeted Risk Assessment
(ECETOC Technical Report No. 93)

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 2004, ISBN/ISSN:
ISBN/ISSN: 0773807293

The Toxicology of Glycol ethers and its Relevance to Man
(ECETOC Technical Report No. 95)

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 2004, ISBN/ISSN: 0773807295

Whole Effluent Assessment
(ECETOC Technical Report No. 94)

European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels 2004, ISBN/ISSN: 0773907294

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