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Bulletin

In this issue

Close to the ‘Picos de Europa’ in the **Asturias National Park** (pictured) in North West Spain is the municipality of **Mieres**, which has a long tradition of mining for coal and metal ores, including those of mercury. A legacy of mercury production in this region is arsenic pollution of surface and other waters. Arsenic toxicity is related to its speciation, which determines bioavailablity. Work on **arsenic speciation**, and its geochemical origins, in two mining areas in Asturias was presented (as a poster) at the **GeoSpec2010** meeting held at Lancaster University in September 2010, and is reported on pp 14–16 of this issue. Five other poster presentations from the Lancaster meeting have also been adapted for this issue: **metal speciation** in the Seine river basin, Normandy, France; **boron speciation** in soil; the impact of metals on the **biodegradation of polycyclic aromatic hydrocarbons** in soil; **soil analysis of a former uranium mine** near St Austell, Cornwall; and kinetic approaches to the chemical **speciation of trace metals** in soils.

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The RSC's Environmental Chemistry Group (ECG) considers all aspects of the complex relationships between chemistry and the environment. The ECG aims to understand the behaviour of chemical species in the water, soil and atmospheric environments; exploring their sources, reactions, transport and in particular their effects on each of these environments.

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This and previous issues of the *Bulletin* are available without charge online at www.rsc.org/ecg. Each member of the Environmental Chemistry Group also receives two issues per year of the printed ECG *Bulletin*. For membership details visit www.rsc.org/Membership.

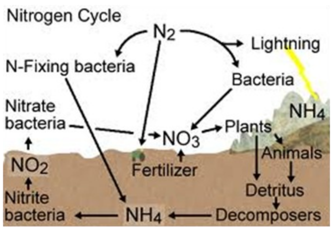
Chairman's report 2010

The Environmental Chemistry Group's traditional activities continued during 2010, but at the end of the year some changes became discernible as the ECG's Chair, **Leo Salter**, explains.

2010 ECG symposia: During 2010, ECG committee members organised a number of successful meetings. Some of these meetings were sole ECG activities, for example March's 2010 Distinguished Guest Lecture and Symposium, and the Atmospheric and Environmental Chemistry Forum, which took place in June. Other events ('Geochemical speciation and bioavailability of trace elements' (GeoSpec2010); 'Contaminated land: chemistry and toxicology aspects of chemical risk assessment', both held in September 2010) were co-organised with other RSC Interest Groups or with other scientific societies.

The RSC supported these meetings with travel grants for speakers and with bursaries for students. Importantly, the Environment, Sustainability and Energy Division (ESED) also provided financial assistance. Without this support some meetings would not have been financially viable. The ECG committee has ambitions to extend its portfolio of meetings and to encourage attendance of students and early career scientists by reducing its registration fees for ECG members.

2011 DGL & Symposium: Nine Earth-system processes and associated thresholds have been identified, which if crossed could trigger unacceptable environmental change: climate change; rate of biodiversity loss (terrestrial and marine); interference with nitrogen and phosphorus cycles; stratospheric ozone depletion; ocean acidification; global freshwater use; change in land use; chemical pollution; and atmospheric aerosol loading (Rockström, J. [+ 28 co-authors], 2009. A safe operating space for humanity. *Nature* **461**, 472-475). Evidence suggests that three of these biophysical thresholds have already been transgressed: climate change; rate of biodiversity loss; and the nitrogen cycle. The implementation of so-called 'planetary boundaries' is recommended as a means of avoiding the environmental consequences of challenging these thresholds. Mankind's interference with the nitrogen cycle – the conversion of atmospheric N_2 into reactive nitrogen species, a consequence of the exigencies of food production – will be the topic of the 2011 ECG Distinguished Guest Lecture & Symposium to be held at Burlington House on March 9th. Professor James Galloway from the University of Virginia will be the 2011 ECG Distinguished Guest Lecturer and has chosen 'Nitrogen: a story of food, feed and fuel' as the title of his talk.



Other 2011 ECG-sponsored symposia: A joint ECG-RSC Historical Group meeting is being planned for October 26th 2011 at Burlington House on 'Environmental Chemistry: A Historical Perspective'. The lives and work of some of the scientists who have influenced our understanding of the chemistry of the atmospheric, terrestrial, and marine environments will be highlighted at this one-day meeting.

ECG *Bulletin*: For the last 16 years (1995-2011) the ECG *Bulletin* and its precursor the ECG *Newsletter* have been edited by Rupert Purchase. Each issue is a high quality publication with content, style and format unique amongst the RSC Interest Groups. Now, after his long and successful tenure in the editorial role, Rupert wishes to step down and this move has stimulated a review of the nature, content, style and management of the ECG *Bulletin*.

The annual cost of publishing two issues of the ECG *Bulletin* a year is around £5K. The work involved in gathering copy, formatting, editing/ proof reading, and then organising the *Bulletin* to be printed and distributed, is not insubstantial. The Committee is therefore looking for one or more new committee members to take on the roles involved in producing the ECG *Bulletin*. Familiarity with desktop publishing software would be an added advantage for prospective committee members.

Rupert's last edition as editor will be January 2011. After that issue, the Committee will be reviewing the publication frequency of the *Bulletin*, and from 2012, for reasons of cost, may only produce one issue per year. Also, in line with RSC policy, the *Bulletin* may only be available in an electronic format, but if at all possible, the Committee would like to continue to support the provision of a printed copy for its members.

Transition of ESEF to ESED: Members may have noticed that ESEF (Environment, Sustainability and Energy Forum) has now acquired Divisional status within the RSC and been renamed the Environment, Sustainability and Energy Division (ESED), reflecting the importance of these three strands of interdisciplinary science for future RSC policy and initiatives. The ECG is one of a number of Interest Groups which report to ESED, and I am currently a member of the ESED Committee in my role as Chair of the ECG.

ESED is committed to pushing forward the RSC's Roadmap* and has identified three priority topics: solar energy; home energy; air quality. Interest Groups which plan and undertake joint activities which support these ESED objectives may approach ESED for financial assistance. This strategy will enhance coherence and communication between RSC Interest Groups and ESED.

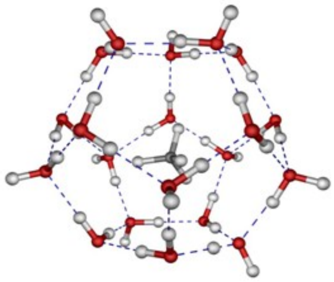
RSC funding for Interest Groups: In 2011, there will be a change in the way Interest Groups are funded. Your annual RSC subscription will cover the costs of Interest Group membership, so this makes it important that ECG members continue to indicate the Environmental Chemistry Group as their Interest Group of choice.

The state of greenhouse gases in the atmosphere based on global observations through 2009: The latest analysis of observations from the WMO Global Atmosphere Watch Programme shows that the globally averaged mixing ratios of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) reached new highs in 2009, with CO_2 at 386.8 ppm, CH_4 at 1803 ppb and N_2O at 322.5 ppb. These values are greater than those in pre-industrial times (before 1750) by 38%, 158% and 19%, respectively. Atmospheric growth rates of CO_2 and N_2O in 2009 are consistent with recent years, but are lower than in 2008. After nearly a decade of no growth, atmospheric CH_4 has increased during the past three years. The reasons for renewed growth of atmospheric methane are not fully understood, but emissions from natural sources (from northern latitudes and the tropics) are considered potential causes. The NOAA Annual Greenhouse Gas Index shows that from 1990 to 2009, radiative forcing by all long-lived greenhouse gases increased by 27.5%, with CO_2 accounting for nearly 80% of this increase. The combined radiative forcing by halocarbons is nearly double that of N_2O. (Source: *WMO Greenhouse Gas Bulletin***,** No. 6: 24 November 2010).

LEO SALTER

December 2010

*RSC Roadmap: http://www.rsc.org/scienceandtechnology/roadmap/index.asp



Methane hydrate: a source of recent rising atmospheric methane levels?

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Geochemical speciation & bioavailability of trace elements (GeoSpec2010)

Six out of the 33 posters which featured at the GeoSpec2010 meeting held at Lancaster University last September have been expanded by their authors into papers for the ECG *Bulletin*. Extended extracts from these six papers appear below and the complete (partly edited) papers accompany the web version of the January 2011 ECG *Bulletin* (www.rsc.org/ecg and links).

Paper 1 Lessons from a large scale deployment of DGT in the Seine basin

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Introduction

The link between the chemical speciation of metals and their toxicity [1] has resulted in a number of different analytical techniques to assess the various fractions of metals present in the aqueous environment. Among these, the Diffusive Gradient in Thin-film technique (DGT), developed by Zhang and Davison [2], is commonly used. DGT is an *in situ* speciation method; it samples a labile fraction composed of free inorganic metals and weakly labile organic complexes. Tusseau-Vuillemin *et al.* [3, 4], and Ferreira *et al.* [5], have shown that this fraction is close to the bioavailable fraction for *Daphnia magna* and aquatic mosses. In addition, DGT is a passive sampling technique, which integrates the metallic contamination during a time deployment of some hours to several weeks. Thus, DGT provides an alternative to spot sampling, which is much more sensitive to concentration fluctuations. For these reasons, passive sampling techniques, and particularly DGT, are gaining acceptance by regulatory and water monitoring authorities.

The main objective of the project presented here was to evaluate the potential of DGT as a monitoring tool on a river basin scale. We present the first results of a large scale deployment of DGT in the Seine river basin. The complete set of measurements constitutes a rich dataset including large and small rivers as well as impacted sites.

DGT samples labile metals, which are free or weakly bound to organic matter (**Figure 1**). Lability is operationally defined i.e. it depends on the thickness and the pore size of the DGT hydrogel. In this study, the use of hydrogels with restricted pore sizes minimized the sampling of large metal complexes.

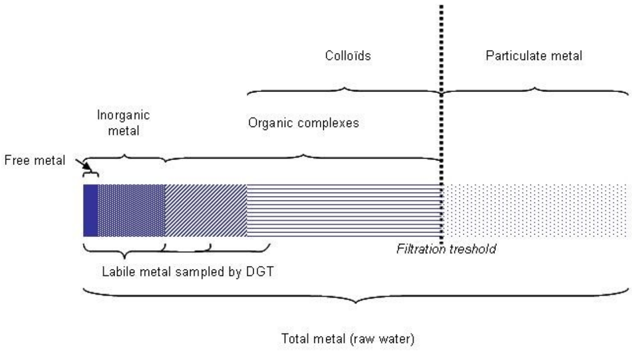

Figure 1: *Metal speciation in a water column.*

Conclusion

The large scale deployment of DGT in the Seine river basin was successful: results from all the samples have been interpreted. A representative data set of labile metal concentrations in an urban-impacted river basin has been produced.

References

See **page 4** for the references for this paper.

Paper 2 On boron in humic and inorganic components of soil: a geochemical *vs.* a chemical approach

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Introduction

Agulhon (1910) first demonstrated boron is an essential element by observing that boron stimulates the growth of several vascular plants in water culture and that boron is abundant in lignified tissue. Maluga (1964) noticed the boron content of plant ash was much higher than that in soils and the lithosphere (400, 10, and 12 mg kg^{-1}, respectively) indicating that boron accumulates in the biosphere. The accumulation of boron varies in different organisms (Bowen, 1966) (**Figure 2**).

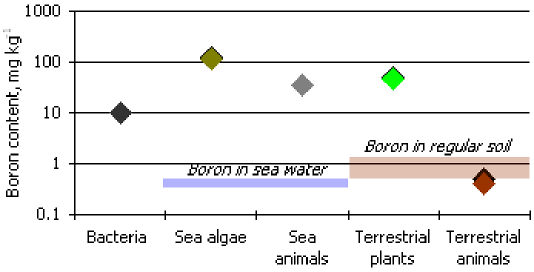

Figure 2: *Boron concentrations in the biosphere.*

It seems that boron is not biomagnified in aquatic food chains, but in the terrestrial food chains, boron accumulates in plants but not in animals (Underwood, 1977). A relatively large amount of circumstantial evidence for the essentiality of boron in animals has been appearing since the 1980s (Woods, 1994; Nielsen, 1998).

Reviews on the fate of boron in soil and soil-plant systems reveal some common, but non-attributable, claims. For example, that boron in soil solution is in the form of inorganic boric acid or borates – depending on the environmental pH – and that these forms are the available forms for plant and bacteria utilisation. This assertion probably originates from the inability of many analytical methods to distinguish between organically-bound and inorganic boron complexes.

According to Kovda (1973), boron is involved in several major soil processes:

- the local soil biological cycle (litter – fresh and partly decomposed);
- the synthesis of humus;
- the formation of clays and the synthesis of colloids;
- illuviation;
- hydrogenic accumulation (meadow soils, solonchaks).

Decomposed and humified plants residues are a major source of organic matter in soil, and soil humus is a principal source of nutrients for vegetation. This plant-soil cycle utilises boron.

Some soil chemistry literature claims that soil boron can be subdivided into: boron in soil solution, adsorbed boron, and mineral boron. And the adsorbed boron is considered in the systems of “soil solution-clay minerals” and “iron/aluminium hydro-oxides”. Such an approach seems questionable, and again can be traced to deficiencies in analytical techniques, which neglect boron-organic matter speciation in their procedures (see Kot, 2007, 2009).

Our preliminary results on soil boron fractionation and potential mobility/bioavailability with special reference to soil humus components lead to the following conclusions:

1. Boron in soil is much more organophilic than is often supposed.
2. Humus components are the principal carriers and determinants of boron species in soil.
3. Mobile boron-water species in soils are elated to colloids of a varied, but probably biotic, origin, not simply to inorganic boric acid or borates, as is often presumed.

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Paper 3 Impact of metals on the biodegradation of polycyclic aromatic hydrocarbons in soil

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are organic substances which contain two or more fused aromatic rings and are common in a wide range of petroleum products, as well as crude oil (Bamforth and Singleton, 2005; Wong *et al*., 2005). They are by-products from incomplete combustion of organic substances such as coal, oil, petrol, and wood, and are ubiquitous in the soil environment (Sokhn *et al*., 2001; Maliszewska-Kordybach and Smreczak, 2003). While concentrations of individual PAHs in soil produced by natural processes are estimated to be around 1-10 µg kg^{-1}, their concentrations in highly polluted soils vary from 10 mg kg^{-1} to 10 g kg^{-1} dry weight (Sokhn *et al*., 2001). PAHs are highly recalcitrant molecules that can persist in soil due to their hydrophobicity and low water solubility, and because some are known to be mutagenic, teratogenic and carcinogenic their fate in nature is therefore of environmental concern. (Sokhn *et al*., 2001; Bamforth and Singleton, 2005).

The persistence of PAHs in soil depends on a variety of factors, for example the chemical structure of the PAH, the concentration and dispersion of the PAH, and the bioavailability of the contaminant. Soil type and structure, pH, temperature, nutrients and water for the activity of the pollutant-degrading microbial community, will all influence the time that PAHs persist in soil (Bamforth and Singleton, 2005).

The association of PAHs with co-pollutants such as heavy metals will also prolong PAH residence time in soil. The presence of heavy metals in soil could inhibit microbial growth and hence limit the metabolism of PAHs in soil.

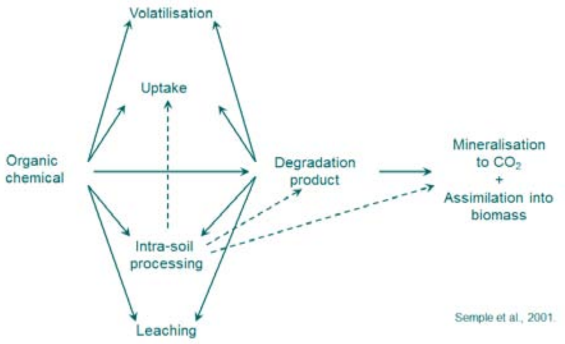
PAHs can be biologically degraded and removed from the natural environment and/or converted into less harmful products by the indigenous microbial community present in a contaminated environment (Bamforth and Singleton, 2005). PAH-degrading microorganisms are ubiquitously distributed in the natural environment, such as soils. These include bacteria such as the genus *Pseudomonas* and *Rhodococcus* as well as fungi such as *Chrysosporium* and *Aspergillus*. However, the presence of heavy metals in soil could adversely affect microflora populations and hence PAH biodegradation.

Metals are ubiquitous in nature and even those metals generally considered as pollutants are found in trace concentrations in the soil environment. Such metals include mercury, lead, arsenic, cadmium, chromium, manganese which are commonly associated with pollution and toxicity, but also include elements (e.g. Zn, Cu and Ni) which are essential in the metabolism of living organisms, albeit at low concentrations (Wong *et al*., 2005). Mining and ore refinement, nuclear processing, and industrial manufacture of a variety of products such as batteries, metal alloys, and fungicides are some of the sources of these metals in the soil environment. These metals in soil can exist as individual metals or more often as metal mixtures and their elevated concentrations in the soil environment have wide-ranging impacts on animal, plant, and microbial species (microbial growth is often slowed or inhibited completely in the presence of excessive amounts of metals) (Roane *et al*., 2005). Due to their toxic nature, the presence of metals in organic-contaminated sites often complicates and limits the bioremediation process.

PAHs and heavy metals are among mixed pollution of major concerns in the soil environment because of the risk they pose to soil health. Soils contaminated with PAHs often contain other pollutants such as heavy metals (HM) this is because often, these contaminants come from same sources (Maliszewska-Kordybach and Smreczak, 2003). Sources of these pollutants in soil include atmospheric deposition, power and heat generation, old gasification and wood preserving plants, metallurgical industries, and fungicide application.

Fate and behaviour of PAHs and metals in soil

Diverse pathways in the soil environment influence the fate and behaviour of both PAHs and metals. PAHs in soil can volatilize, be leached, complex with soil minerals and organic matter, biodegrade to CO_2, or undergo carbon assimilation by the microbial biomass (**Figure 3**). Metals can be removed by volatilization, and when in an aqueous phase, losses can be a result of plant uptake, surface runoff, complexation or sorption to minerals and organic matter, and precipitation of the metal salt.



Semple et al., 2001.

***Figure 3:** Fate and behaviour of an organic chemical (e.g. a PAH) in soil.*

Ageing of PAHs and metals in soil is a major factor in determining their bioavailability, because of the affinity these co-contaminants have for soil organic matter and clay content. In well-aged soils, mild extractability, bioavailability and biodegradation assays for PAHs are usually low (Stokes *et al*., 2005). Ageing of metals in soils has been demonstrated to be a major factor in determining their bioavailability or lability, with bioavailability decreasing with increases in metal-soil contact times (Wendling, 2009). Several processes contribute to metal ageing in soils including incorporation into mineral structures, diffusion into pore spaces within minerals, nucleation or precipitation, mineral surface oxidation and entrainment *via* the formation of chemical complexes with soil solids (Wendling *et al*., 2009).

Metal toxicity to the microbial cell

Metals are essential components of microbial cells; for example, sodium (Na) and potassium (K) regulate gradients across the cell membrane, and copper, iron and manganese are required for the activity of key metalloenzymes in photosynthesis and electron transport (Roane *et al*., 2005). However, metals can also be extremely toxic to microorganisms (especially at high concentrations) impacting on microbial growth, morphology and biochemical activities as a result of specific interactions with cellular components (Giller *et al*., 1998; Wong *et al*., 2005). This toxicity of metals towards microorganisms affects the degradation of PAHs in soil.

Mechanisms of metal toxicity differ. Toxicity may occur as a result of binding of the metal to ligands containing sulfhydryl, carboxyl or phosphate groups such as proteins or nucleic acids (Roane *et al*., 2005). Mercury (Hg) and cadmium (Cd) cations readily bind sulfhydryl groups causing protein synthesis inhibition (**Figure 4**). It could also be as a result of metal-catalyzed decomposition of essential metabolites and analogue replacement of structurally important cell components. A good example is arsenic (As), which is bactericidal because it acts as an analogue of phosphate, disrupting nucleic acid structure and enzyme action (**Figure 4**) (Roane *et al*., 2005). High concentrations of lead (Pb) and nickel (Ni) retard cell division, while copper (Cu) and zinc (Zn) cause cell membrane disruption (**Figure 4**).

A wide range of soil properties such as pH, organic matter content, clay content, iron oxide content and redox potential affect soil metal concentrations and hence the impact of metals on soil microbes (Giller *et al*., 1998). Of these, pH has the greatest influence because pH determines the solubility and speciation of metals in soil. The free metal ion is generally assumed to be the chemical species which is taken up by soil microbes and is toxic when present in an excess (Giller *et al*., 1998).

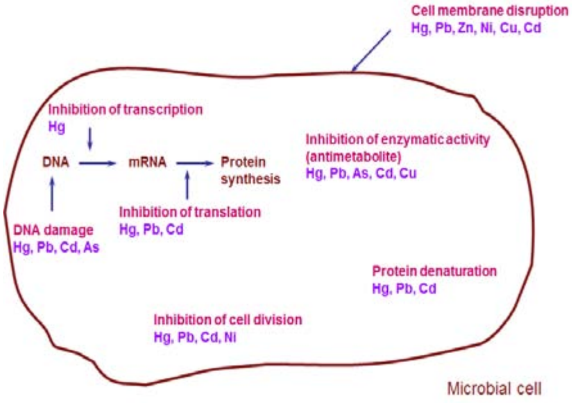


Figure 4: *Mechanisms of metal toxicity to a microbial cell.*

These negative effects of heavy metals on soil microbes and soil microbial processes can potentially limit the bioremediation of organic pollutants. Examples from the literature include:

- Decreases in phenanthrene degradation, microbial respiration and microbial numbers with increasing concentrations of Cu (Sokhn *et al.*, 2001; Obuekwe and Semple, 2011).
- Inhibition of phenanthrene biodegradation and microbial metabolic activity at high Zn concentrations (Wong *et al.*, 2005).
- Decrease in PAH biodegradation and mycelial soil colonization in Cd–PAH–contaminated soils (Baldrin *et al*., 2000).
- Lower microbial count and CO_2 evolution in soil in the presence of PAHs and cupric sulphate ($CuSO_4$). This is thought to be as a result of inhibition of microbial growth and metabolism in the presence of $CuSO_4$ (Atagana, 2006).

Methodologies for studying PAHs and metals in the laboratory

Techniques for studying soils contaminated with PAHs and metals in the laboratory examine:

(a) **PAH degradation** (b) **microbial activity** (respiration, enzyme activity *etc.*) and (c) **microbial population**. The PAH–metal(s) co-contaminant mixtures may be either artificially simulated in the laboratory or soils already contaminated with the co-contaminants in the environment are used. The co-contaminants are incubated in the presence of indigenous microflora or introduced inocula for a period of time after which PAH degradation, microbial activity as well as bacteria count and/or fungal soil colonization are assessed.

Techniques for analysing **PAH degradation** include: solvent extraction and GC (Sokhn *et al*., 2001); solvent extraction and GC-MS (Baldrin *et al*., 2000; Wong *et al*., 2005); conversion of ^{14}C PAH into $^{14}CO_2$ using respirometry (Semple *et al*., 2001; Obuekwe and Semple, 2011). **Microbial activity** can be assessed by measuring CO_2 evolution with an infrared CO_2 analyser (Sokhn *et al*., 2001) or $^{14}CO_2$ evolution using respirometry (Semple *et al*., 2001; Obuekwe and Semple, 2011). Microbial metabolic activity can also be determined by measuring various enzyme activities (Wong *et al*., 2005; Baldrin *et al*., 2000). **Microbial populations** may be examined using a bacteria plate count technique (Sokhn *et al*., 2001; Atagana 2006; Obuekwe and Semple, 2011). Fungal soil colonization can be used to assess fungal soil growth (Baldrin *et al*., 2000).

Factors that influence the impact of metals on PAH biodegradation in soil

Soil type: Soil pH has the highest influence on metal toxicity because of its impact on metal solubility and speciation in soil. Soils with low pH usually contain metals in a more soluble form resulting in enhanced metal bioavailability and toxicity. For example, Wendling *et al*., (2009) found an increase in isotopically exchangeable cobalt in acidic soils compared with neutral or alkaline pH. Biodegradation of PAHs in the presence of metals in soil with a low pH could therefore be impeded.

Organic matter content, clay content, and cation exchange capacity (CEC) are other soil properties that affect metal toxicity. Low lability of Cu in soils with high organic matter has been reported (Ma *et al*., 2006). Finer textured soil, which is much higher in clay content and cation exchange capacity, possesses a greater binding ability for added metals than coarse-textured soil (Kim *et al*., 2008).

Metal ageing in soil: Ageing of metals in soils is a major factor in determining their bioavailability and toxicity, with metal bioavailability decreasing as metal-soil contact time increases. For example, a decrease in the readily soluble and weakly sorbed Co pools in soils with time has been reported (Wendling *et al*., 2009). Recent unpublished research (Obuekwe and Semple, 2011) on the impact of Zn or Cu on phenanthrene catabolism in soil showed significant increases in phenanthrene catabolism at high Cu concentration (500 mg kg^{-1}) with time [also *vide infra*]. This could be as a result of Cu diffusing into nanopores or interstices and becoming less bioavailable to prevent phenanthrene catabolism in soil.

Metal concentration in soil: Heavy metals are known to be potentially toxic to soil microorganisms at high concentrations and can hinder the biodegradation of organic contaminant in soil (Wong *et al*., 2005). Many studies have reported an increase in metal toxicity with increasing concentration; Cu at concentrations of 700 and 7000 mg kg^{-1} soil were found to reduce microbial activity and phenanthrene biodegradation (Sokhn *et al*., 2001). Raised Zn concentrations in soil (720 and 1440 mg kg^{-1}) inhibited both phenanthrene biodegradation rates and microbial metabolic activity. High Cu concentrations (500 and 1000 mg kg^{-1}) reduced microbial numbers and phenanthrene biodegradation in soil (Obuekwe and Semple, 2011) [also *vide supra*].

Metal speciation: The potential toxicity of a heavy metal in soil depends upon its speciation and availability. Heavy metals are present in various forms with different degrees of mobility and bioavailability. The toxicity of a heavy metal can be linked to its free-ion activity (Chaperon and Sauve, 2008; Kim *et al*., 2008). Kim *et al*., (2008) provided evidence that Cu^{2+} was a better surrogate for estimating the toxic effect of Cu than Cu extractable by $CaCl_2$. Free Cu^{2+} ion is the likely toxic species of Cu, reacting directly with sulfhydryl groups on the active site of the enzyme (dehydrogenase) and causing its inhibition. Metal speciation in soil is influenced by a number of physico-chemical properties including soil pH, clay and organic matter content, Fe and Mn oxide composition and content, as well as long term fixation or ageing effects (Wendling *et al*., 2009).

Conclusion

Heavy metals at elevated concentrations in the soil environment have a range of effects on microbial species. These include a decrease in microbial count and disruption of nucleic acid and enzyme function, which subsequently reduce or impede the biodegradation of PAHs in soil. Heavy metal toxicity in soil depends on factors which affect their interaction with PAHs. Due to their toxic nature, the presence of metals in PAH–contaminated land sites can often complicate and limit bioremediation processes.

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Paper 4 Characterisation of soils containing naturally occurring radioactive material (NORM) using *in situ* and rapid laboratory techniques. Case study: South Terras, Cornwall.

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Introduction

In situ analysis has become increasingly important for contaminated land investigation and remediation. At present, portable techniques are used mainly as scanning tools to assess the spread and magnitude of the contamination, and are an adjunct to conventional laboratory analyses. A site in Cornwall, containing naturally occurring radioactive material (NORM), provided an opportunity for Reading University PhD student **Anna Kutner** to compare analytical data collected *in situ* with data generated by laboratory-based methods. The preliminary results in this paper extend the author's poster presentation at last September's GeoSpec2010 conference held in Lancaster.

Case study site: South Terras, Cornwall

South Terras is a historical mining site located to the west from St Austell in the valley of River Fal, Cornwall. The area has a strictly metaliferrous character, located directly on a tin and uranium vein, hence there is a long history of mining activities, which can be roughly divided into: iron–tin mining (1870–1890s), uranium mining (1890s–1910s), and radium extraction works (1910s–1930s) [1, 2]. After closure in the early 1930s, the site has been left undisturbed and currently has a SSSI status (Sites of Special Scientific Interest) due to the occurrence of rare minerals. Consequently South Terras provides an ideal environment for research on the behaviour of natural radionuclides in a post-industrial environment. [See also http://www.dangerouslaboratories.org/rcw3.html for further details of the location].

Methodology

Techniques selected to assess the South Terras site are shown in **Table 1**.

***In situ* techniques**	**Laboratory-based techniques**
Geiger counter	Gamma spectroscopy
Radon detector (RAD7)	Infrared (IR) techniques
Portable X-Ray Fluorescence (PXRF)	X-Ray Diffraction (XRD)
Groundhog (GH)	X-Ray Fluorescence (XRF)
Portable gamma spectroscopy	ICP-OES

Table 1: *The range of techniques employed to assess the South Terras mining site.*

The techniques aim to determine: the distribution of gamma-emitting radionuclides at the site (Groundhog), characterise the nature of NORM contamination present at the site/in the samples (gamma spectroscopy), radon in ambient air (RAD7), composition of the surface of buildings still remaining at the site (PXRF, excluding radium), elemental composition (XRF, ICP-OES) and mineralogy of the topsoil (XRD, IR) based on the samples collected during the first field trip in April 2010. An additional aspect of this project will involve a comparison of the methods employed in terms of their accuracy and precision, duration of analysis, and portability.

Preliminary observations and results

Radon measurements were conducted throughout the site, which established that the average concentration of radon in the ambient air was between 100-300 Bq m^{-3}. However, in the northern corner of the site the radon exhalation reached a level of 16,000 Bq m^{-3} (using RAD7). This is likely to be an indication of the location of the Northern Shaft, not recorded on current OS maps (**Figure 5**, Mark A). The Geiger counter proved to be a useful tool to roughly indentify “hot spots”, especially in the woodlands where the GPS signal used by the Groundhog system was lost. The areas of elevated radiation correlated perfectly with the historical location of the ore processing and extracting units (data for those finding will be reported at a later date). The buildings located at the site still contain some level of surface contamination. The highest readings between 550-800 cps were recorded for the walls of Building A (**Figure 5**, Mark B) (background at the site ~40-60 cps). The building was considered to be an office/storage unit, however the concentration of U above 200 ppm (PXRF) indicated that the building material used for construction contained materials enriched in uranium and thorium, possibly the spoil material from the industrial processes at the site. Slime tanks (**Figure 5**, Mark C) located behind Building A contain radium-contaminated waste deposited there after the closure in 1930s. It is assumed that waste slurry was mixed with wet concrete and covered with a concrete slab for better shielding. Uranium levels on the surface of the slab were below LOD (PXRF), but a radon peak was recorded (>270 Bq m^{-3}), which might indicate imperfections in the concrete structure (e.g. formation of cracks) or improper mixing application and emanation of radon from the decay of radium contained in waste.

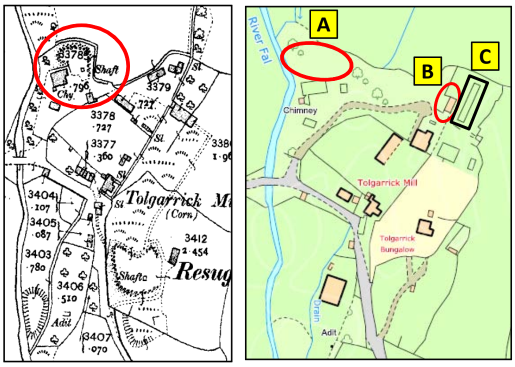

Figure 5: *Detailed maps of South Terras from 1907 (left) and 2010 (right, with marked “hot spots”) [3].*

Mineralogy of the site comprises quartz (SiO_2) and hematite (Fe_2O_3), as well as calcite ($CaCO_3$) and aluminosilicates, especially kaolinite, the presence of which is to be expected considering the proximity of china clay located just a few miles north from South Terras, where mineral used to be excavated for production of porcelain and, more recently, fine grade paper. Samples have high organic content which might provide a natural sink for some radionuclides due to complexing properties of humic and fulvic acids [4, 5].

Discussion

Due to the local geology, the study area is naturally enriched in U and Th. However, industrial activity has exposed the surface soils to high-grade uranium ore (approx. 36%) [1] comprising pitchblende and uraninite (UO_2-U_3O_8), as well as the products of ore extraction and processing procedures. As expected, the samples collected in the vicinity of extraction and smelting facilities were enriched in radionuclides from ^{238}U and ^{232}Th decay chains, all levels within the limits set by Schedule 23 in the Environmental Permitting regulations (2010) (previously Schedule 1 in the Radioactive Substances Act 1993).

The presence of calcite ($CaCO_3$) and hematite (Fe_2O_3) at the site might indicate a potential for entrapment of radium bivalent ion Ra^{2+} by substitution for calcium in calcite due to common origin as earth alkaline elements or formation of insoluble complexes with iron oxides [6]. Uranyl ion (UO_2^{2+}) forms highly soluble complexes with carbonates over a wide range of pH, thus there is a potential for leaching of U into groundwater or transport in the run-off to the nearby River Fal.

However, on the entry points to the River Fal no increase in the concentration of uranium in water has been observed, since the main fraction of the radionuclide is bound to the sediments [7]. Additionally, the enhanced presence of organic matter is another potential mechanism for immobilisation of radionuclides due to the complexing properties of humic and fulvic acids. Those properties are being investigated more fully as a part of the research about the construction of a deep geological repository in United Kingdom to store intermediate and high level waste [4, 5].

Summary

This paper presents our preliminary findings at South Terras. During the early part of 2011 we will complete the data acquisition and interpretation to provide a fuller picture of this site. These results will be complemented by historical data obtained from the Cornwall Record Office on the type of extraction techniques employed at South Terras from *ca.* 1870–1930.

Acknowledgments

I thank Nuvia for the loan of the Groundhog^{TM} system and Dr Black and Dr Almond for their help during the first field trip. I am grateful to the Boconnoc Estate for allowing me access to South Terras, and I thank Dr Imad Ahmed for inviting me to submit this article to the ECG *Bulletin*.

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Paper 5 The Interest of Kinetic Considerations in Soil Heavy Metal Mobilization Assessment: An Overview

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Introduction

Many agricultural and industrial activities such as sewage sludge, wastewaters, fertilizers, and smoke from factories result in trace metal pollution of soils. The deleterious effects of this contamination on the biota are of concern. However, it is known that the total concentration of a metal in soil is not a reliable indicator of its potential ecological risks. Current research in metal speciation in soil/solution systems attempts to determine the part of metal that is available to biota. Various single and sequential chemical extraction schemes have been devised to assess "reactive" or "labile" pools of metal in the soil solid phase (e.g. Barona and Romero, 1996; Tipping *et al.*, 2003; Mocko and Waclawek, 2004; Feng *et al.*, 2005; Young *et al.*, 2006; Manouchehri and Bermond, 2009).

However, in most of these extraction methods, the metal concentration is measured at equilibrium whereas natural systems are generally subject to changing conditions and are not at equilibrium. For these dynamic systems, metal availability is thought to be controlled by kinetic factors (Errecalde *et al.*, 1998; Ma *et al.*, 1999; Fortin and Campbell, 2000; Hassler and Wilkinson, 2003; Slaveykova *et al.*, 2003).

New techniques have been introduced to meet the challenge of understanding speciation in dynamic metal–soil/water systems. For example, **kinetic fractionation** (Bermond *et al.*, 1998; Fangueiro *et al.*, 2002; Bermond *et al.*, 2005; Wasay *et al.*, 2007) and **Diffusive Gradients in Thin-films** (**DGT**) (Zhang *et al.*, 1995; Harper *et al.*, 2000). Information on the dynamic behaviour of metals in the soil solid phase and their concentrations in pore solution is helpful for soil remediation procedures, the prediction of metal bioavailability, and risk assessment in general.

[In the accompanying web version of this paper, kinetic fractionation methods and developments in DGT are reviewed, and a soil/solution/resin batch model is used to illustrate kinetic monitoring.]

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Views of the South Terras mining site, Cornwall. (Paper 4)

Paper 6 Speciation and distribution of arsenic for studies of availability and mobility in mining environments

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Introduction

Arsenic is the twentieth most abundant element in the earth's crust. It is a toxic trace element naturally present in all terrestrial and aquatic environments. High arsenic levels in water and soil endanger human health. Normal arsenic levels in soils range from 1 to 40 mg kg^{-1} [1], although some anthropogenic and volcanic activities can raise this upper limit. Various arsenic compounds are present in the environment and in biological systems [2]. Inorganic forms (arsenate and arsenite) are the predominant species, and at lower concentrations, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are found.

Arsenic toxicity depends on its speciation. Trivalent arsenic compounds are considered to be more toxic than pentavalent arsenic compounds. An approximate order of decreasing toxicity is as follows: $R_3As > As(III) > (RAsO)_n > As(V) > R_2AsO(OH) > R_4As^+ > As(0)$; R = H > alkyl > aryl. Physicochemical and environmental factors such as pH, redox potential, absorption-desorption processes and the presence of microorganisms contribute to arsenic speciation and toxicity.

The work described in this paper focuses on mercury mining areas in Asturias, a Spanish region with a historical tradition in mining and mineral processing. In particular, the extraction of mercury ores with a high arsenic content was quite widespread. As a result of these activities and related mechanical and chemical dispersion, significant amounts of arsenic have been released into the environment. Hyphenated analytical techniques are used to determine the extent and nature of arsenic pollution in the region.

Sampling area

The area we studied for this paper is located in Asturias (Northern Spain). Mieres and Pola de Lena are two districts where important mercury mines were exploited for decades and are nowadays abandoned. Three important mines belong to these areas: "La Soterraña", "La Peña-El Terronal" and "Los Rueldos" and were part of our study.

An abandoned mercury mine at Mieres, Asturias

Asturias was an important location for the production of mercury during the decade 1962-1972, with average annual productions of 15,000 flasks [3]. "La Peña-El Terronal" and "La Soterraña" were the most productive mines, located in Mieres and Pola de Lena districts, respectively, both in Central Asturias. The mines closed between 1973 and 1974 leaving a legacy of abandoned underground mines, extraction machinery and spoil heaps. In these Hg-mineralized areas, As is present in the form of As-rich pyrite, orpiment, realgar and occasionally arsenopyrite. Mine drainage and leachates from spoil heaps are often acidic with elevated As levels, leading to pollution of the Caudal River tributaries.

Arsenic speciation in mining waters

Arsenic is a common constituent of many metal ores and a trace element in sulphides associated with waste deposits from mining activities. Both natural and accelerated weathering of these arsenic-bearing materials results in the release of arsenic into the waters. The concentration of As in unpolluted waters typically ranges 1-10 µg L^{-1} [4]. However, arsenic levels in water in exploited sulphide mineralization areas can be extremely high. In Asturias, arsenic concentrations up to 57,000 µg L^{-1} have been found [5].

Speciation analysis [6] indicates that inorganic arsenic species, As(III) and As(V), prevail in natural waters, especially in sulphide oxidation environments [7]. Methylated compounds, monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) are not quantitatively important, and are only present in waters affected by industrial pollution [8].

Speciation of inorganic arsenic is a function of pH and redox potential (**Figure 6**). Under oxidising conditions at pH less than 6.9, $H_2AsO_4^-$ is dominant; at higher pH $HAsO_4^{2-}$ predominates. H_3AsO_4 and AsO_4^{3-} are present in extremely acidic or alkaline conditions, respectively. Under reducing conditions at pH less than 9.2, the uncharged arsenic species H_3AsO_3 prevails. At moderate or high redox potentials, As may be present as pentavalent oxyanions (arsenate): H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$, and AsO_4^{3-}. However, under more reducing conditions (acidic and mildly alkaline) and lower redox potential, trivalent arsenic species (H_3AsO_3) are found [9, 10].

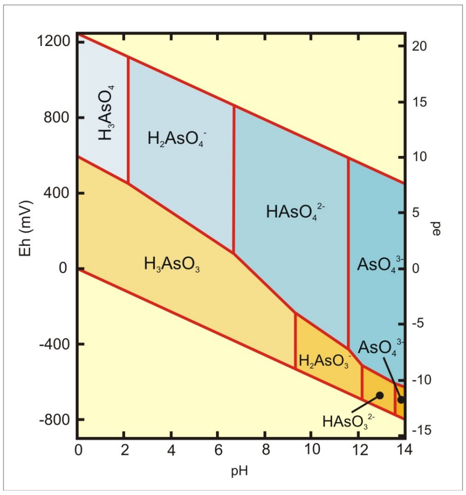

Figure 6: *Eh-pH diagram for arsenic(III) and arsenic(V) oxyanions.*

In mining sites, acid mine drainage (AMD) is responsible for the release of relatively high levels of arsenic into surface and other waters. The high acidity generated during the oxidising processes gives rise to accelerated hydrolysis of minerals in the spoil materials, causing large quantities of the constituent elements to solubilise [11]. Arsenic minerals are associated with iron oxides or hydroxides, and a relationship between arsenic and iron speciation has been observed [11]. Correlations between the As(III)/(V) ratio and Fe(III) concentrations have been reported in waters from rivers affected by AMD. Also there is an inverse relationship between dissolved sulphate and arsenic which means that mobilisation of arsenic is not caused by oxidative dissolution of pyrite [12].

Analytical techniques for determining arsenic species

High-performance liquid chromatography is widely used for the analysis of arsenic species. Buffers (mainly phosphate buffers) are usually employed as mobile phases at different pH values ranging from 4.5 to 8.5, and they can be used both in isocratic and in gradient modes [13]. For the separation of cationic species, cationic exchange columns are used e.g. Hamilton PRP X-200 [14] and Supelcosil LC- SCX [15]. For the determination of all species, two columns of different nature can be placed in parallel [16]. A favoured option for the separation of many arsenic compound is a Dionex Ion Pac As7 column [17]; separation of As(III), MMA, DMA, As(V), AsB, TMAO, AsC, TMA can be achieved within 14 minutes with nitric acid as a mobile phase in gradient mode.

For detection, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is commonly used, since it provides a great sensibility, multi-elemental capability, and large dynamic range. And coupling with HPLC is relatively easy, because the usual flow rates for HPLC are totally compatible with the uptake flow rate of an ICP system.

Hydride generation (HG), followed by spectrometry, is also popular. This technique is based on the formation of volatile hydrides by means of chemical treatment of a sample with a reducing agent, typically sodium borohydride. The advantage of this method is that the target arsenic species can be separated by volatilization from almost all other accompanying constituents in the sample through the HG process, so spectral and chemical interferences encountered in the detection systems are essentially eliminated. However, one drawback is that several organoarsenic compounds do not form volatile hydrides, so derivatisation methods to convert them into hydride-forming species are necessary. Microwave-assisted oxidation [18] and UV photo-oxidation [19] with potassium persulphate and sodium hydroxide have been used successfully for this task. Among the possible spectrometry techniques, atomic fluorescence (AFS) is the most attractive one, given its lowest detection limits.

For our field work in Asturias, HPLC-HG-AFS was the technique selected for the analysis of waters at the three mining sites. We showed that the four more common arsenic species could be separated using the technique (**Figure 7**), but in the actual samples from the Asturian mining sites, only inorganic species were found (**Figure 8**).

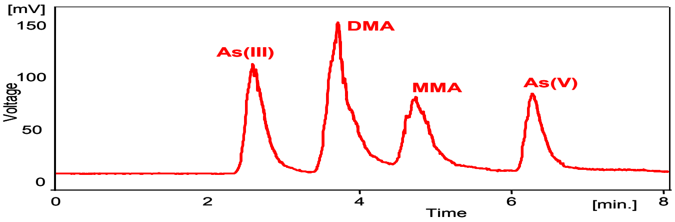

Figure 7: *Chromatogram showing the separation and identification of four arsenic species using HPLC-HG-AFS.*

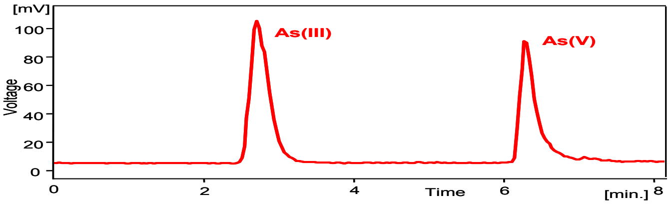

Figure 8: *Chromatogram of the arsenic species found in Asturian mining samples using HPLC-HG-AFS.*

As (V) was the only species found in all the samples from the three mining sites. This is agreement with the Eh-pH diagram, given the Eh and pH value of our samples (Soterraña: Eh~200mV, pH~8; La Peña-El Terronal: Eh~200mV, pH~8; Los Rueldos: upstream, before the mine: Eh~100mV, pH~7; downstream, after the mine: Eh~600, pH~3).

The most elevated arsenic concentrations occur at La Soterraña mine (~43,000 µg L^{-1}). Arsenic concentration is lower at La Peña-El Terronal (~1600 µg L^{-1}). This mine was subject to preventive measures in 2002 when spoil heap wastes from tailings were segregated in a secure landfill site to avoid the formation of leachates. The influence of AMD is evident in the Los Rueldos mining site. Samples collected upstream had low As concentrations. Here the waters are at neutral pH and oxidative capacity and heavy metal concentrations are low. Downstream from the spoil heap the aqueous environment is altered, solubilisation of heavy metals occurs and arsenic levels are raised (~10,000 µg L^{-1}).

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16. Kuehnelt, D.; Goessler, W.; Irgolic, K. J. (1997). Arsenic compounds in terrestrial organisms: II. Arsenocholine in the mushroom amanita. *Appl. Organomet. Chem.*, **11**, 459-470.
17. Londensborough, S.; Mattusch, J.; Wennrich, R. (1999). Separation of organic and inorganic arsenic species by HPLC-ICPMS. *Fresenius J. Anal. Chem.*, **363**, 577-581.
18. Lamble, K. J.; Sperling, M.; Welz, B. (1996). Arsenic speciation in biological samples by on-line high performance liquid chromatography-microwave digestion hydride generation-atomic absorption spectrometry. *Anal. Chim. Acta* , **334**, 261-270.
19. Zhang, X.; Cornelis, R.; de Kimpe, J.; Mees, L. (1996). Arsenic speciation in serum of uraemic patients based on liquid chromatography with hydride generation atomic absorption spectrometry and on-line UV photo-oxidation digestion. *Anal. Chim. Acta*, **319**, 177-185.

Meeting report

RSC Environmental Chemistry Group Atmospheric and Environmental Chemistry Forum

The EGC held its second Forum for PhD students and post-doctoral researchers at Burlington House on 4th June 2010. The Forum's subject area was expanded from last year's inaugural meeting to include atmospheric *and* environmental chemistry. However, the Forum's aims remained the same: to provide atmospheric/ environmental chemists at the start of their research careers with an opportunity to present their work to an audience of their peers, to exchange knowledge and hence build links between research groups, and to discuss career prospects in the area. Below we present a selection of scientific abstracts from the Forum.

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1. Measurement of the product branching ratios of selected ozone + alkene reactions using photoelectron spectroscopy

G. Copeland[1], J. M. Dyke[1], and D. E. Shallcross[2]

1. Department of Chemistry, Southampton University

2. School of Chemistry, Bristol University

Ozone's reactions with alkenes are important sources of free radicals (including OH) and particulate material in the Earth's atmosphere. A particular area of interest concerns the chemical mechanisms and product branching ratios of the ozonolysis of alkenes.

This work studied three ozone + alkene reactions as a function of reaction time using a flow-tube interfaced to a photoelectron (PE) spectrometer. The alkenes chosen were ethylene, 2-methylpropene (2MP) and tetramethylethylene (TME). The products observed from the reactions were acetaldehyde, formaldehyde, acetone, formic acid, O_2, CO_2 and CO (see **Figure 1**). Photoionisation cross-sections (PI-CS) of the first bands of the reactants and products observed in the PE spectra were measured relative to argon at the He(I) photon energy (21.22eV).

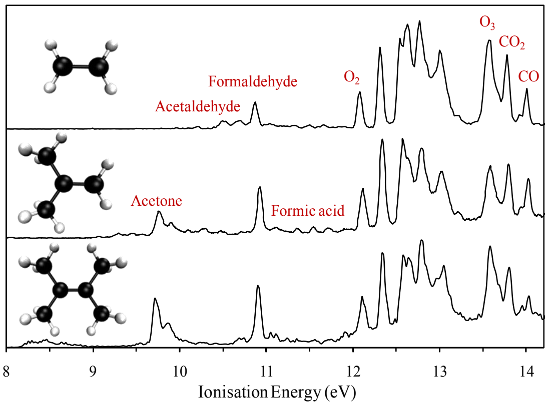

Figure 1: *Photoelectron spectra showing the products observed from selected ozone + alkenes reactions.*

The measured PI-CSs were used along with measured PE band intensities to plot the absolute partial pressures of reactants and products as a function of reaction time for each alkene, in order to determine the reaction branching ratios. These reaction branching ratios have been used in global model simulations in order to determine the amount of products produced per year in the atmosphere and thus to gain a better understanding of the atmospheric implications of the results.

2. Kinetic and thermochemical studies of the ClO + ClO self-reaction

Valerio Ferracci and David M. Rowley

Department of Chemistry, University College London

Work by von Hobe *et al.* published in 2007 [1] challenged the then current understanding of the ClO dimer's role in catalytic cycles leading to stratospheric ozone loss. Our study focuses on the temperature dependence of the equilibrium constant of one of the key reactions in this process, $ClO + ClO + M \leftrightarrow Cl_2O_2 + M$ (1, −1). ClO radicals were generated *via* laser photolysis of Cl_2/Cl_2O/air mixtures and monitored *via* ultra-violet absorption spectroscopy using a CCD camera. The equilibrium constant was determined from the ratio of forward and backward rate coefficients $K_{eq}=k_1/k_{-1}$ over the temperature range T = 256.55–312.65 K. **Figure 2** compares the temperature dependence of the equilibrium constants from this work with previous studies.

The standard enthalpy and entropy changes of reaction (1), $\Delta_rH°$ and $\Delta_rS°$, were obtained from the measured K_{eq} values using analyses based on the Second and Third Laws of thermodynamics. The Second Law analysis gave $\Delta_rH° = -80.7 \pm 2.2$ kJ mol^{-1} and $\Delta_rS° = -168.1 \pm 7.8$ J K^{-1} mol^{-1}, whilst a Third Law analysis gave $\Delta_rH° = -74.65 \pm 0.4$ kJ mol^{-1} and $\Delta_rS° = -148.0 \pm 0.4$ J K^{-1} mol^{-1}. These values agree with previous work by Nickolaisen *et al.* [2] but are greater in (negative) magnitude than current recommendations commonly used in atmospheric modelling [3].

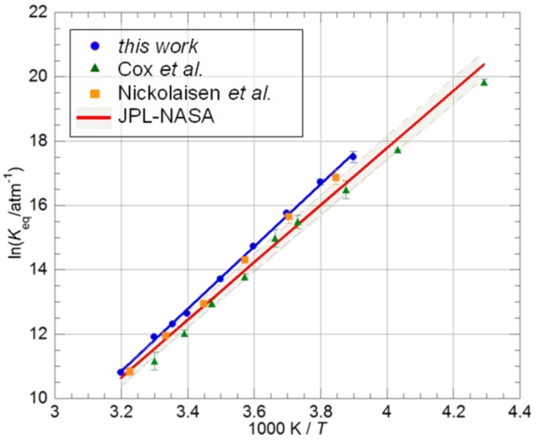

***Figure 2:** A van'T Hoff plot for the thermodynamics of ClO dimer formation.*

Rate coefficients for two of the three bimolecular product channels of the ClO self-reaction were also characterised for temperatures T = 298.15–323.15 K:

$$ClO + ClO \rightarrow Cl_2 + O_2 \quad (1b)$$

$$k_{1b} = 2.9\times10^{-14} \exp[-283/T]$$

$$ClO + ClO \rightarrow OClO + Cl \quad (1d)$$

$$k_{1d} = 7.2\times10^{-15} \exp[-225/T]$$

The above Arrhenius expressions for channels (1b) and (1d) are, respectively, greater than and in good agreement with previous work [2].

[1] M. von Hobe *et al.*, *Atmos. Chem. Phys.*, 2007, **7**, 3055.

[2] S. L. Nickolaisen, R. R. Friedl, S. P. Sander, *J. Phys. Chem.*, 1994, **98**, 155.

[3] S. P. Sander *et al.*, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*, JPL Publication 06-2, NASA Jet Propulsion Laboratory, Pasadena, 2006.

3. Hydrocarbon ratios: a useful tool for interpreting chemical and transport processes in the atmosphere

Shalini Punjabi, James R. Hopkins, and Alastair C. Lewis

Department of Chemistry, University of York

Whole Air Samples collected during various atmospheric field campaigns between 2009 and 2010 have been used to measure the mixing ratios of volatile organic compounds (VOC) above the UK. Boundary layer, including urban plumes, and free tropospheric samples were collected during day and night flights aboard the Facility for Airborne Atmospheric Measurements' BAe 146 research aircraft. Samples were analysed for C_2 to C_8 VOCs using a dual-channel gas chromatograph coupled with flame ionisation detection (GC-FID).

Current work focuses on the use of hydrocarbon ratios as a tool to interpret chemical and transport processes. The role of nitrate radical chemistry has been assessed by comparing VOC data from day and night flights. These data clearly indicate a deviation from hydroxyl chemistry and an increasing influence of the nitrate radical initiated VOC oxidation at night. In addition, long-term measurement of free tropospheric VOC concentrations indicates a clear seasonal trend with winter maxima and summer minima, confirming the role of hydroxyl chemistry as the dominant sink for most VOCs during the daytime.

4. Atmospheric impacts of biofuel feedstock cultivation

Kirsti Ashworth[1], O. Wild[1], C. N. Hewitt[1], and G. Folberth[2]

1. Lancaster Environment Centre, Lancaster University

2. Met Office Hadley Centre

Emissions of volatile organic compounds from the global biosphere (bVOCs) are estimated at 1150 TgC/yr, nearly an order of magnitude higher than anthropogenic fluxes. The most significant of these bVOC compounds is isoprene (C_5H_8) which has emissions of around 500 TgC/yr and is highly reactive, with an atmospheric lifetime of about 1.5 hours. Isoprene oxidation provides a source of peroxy radicals that fuel production of tropospheric ozone, and leads to formation of aerosol particles. Ozone and aerosols impact both air quality and climate.

Emissions of bVOCs are plant species dependent and highly sensitive to the global distribution of vegetation. Land use change (LUC) is expected to alter the magnitude and spatial distribution of emissions, and hence affect the production of ozone and aerosols. This study uses the HadGEM2-ES model to investigate the impact on air quality and climate of LUC associated with cultivation of biofuel feedstocks. The scenarios investigated are based on near-future government policies focusing on the expansion of oil palm plantations in the tropics, and the cultivation of short rotation coppice species at mid-latitudes.

Preliminary results (e.g. **Figure 3**) show that surface ozone and biogenic secondary organic aerosol increase in the regions of the new biofuel plantations, indicating that cultivating biofuel feedstocks can have detrimental impacts on air quality.

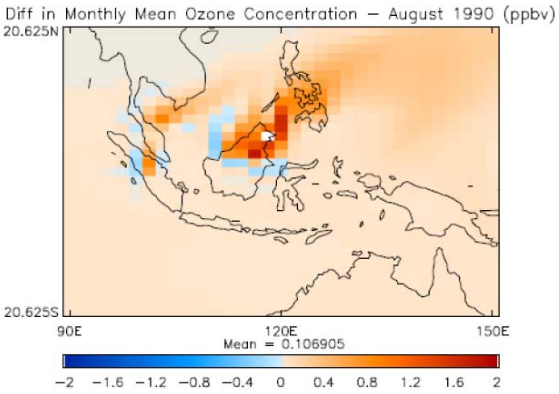

Figure 3: *A prediction of near-future surface ozone changes in SE Asia resulting from conversion of 27.4 Mha of rainforest to oil palm plantations (under current climate and anthropogenic emissions).*

5. Aerosol and the oxidative capacity of the urban atmosphere

Iain C. A. Goodall, Stephen M. Ball, Paul S. Monks, and Iain R. White

Department of Chemistry, University of Leicester

Organic aerosols are produced in the atmosphere by photochemical particulate formation, and are known to have detrimental effects on air quality (and thus human health) and local climate. Many of the oxidized volatile organic compounds (OVOCs) that deposit onto existing aerosol, or condense to form secondary organic aerosols (SOA), are toxic and/or carcinogenic. So to establish SOA's impacts upon human health, it is vital to be able to monitor and understand SOA formation in a range of environments. Our research investigates the chemistry and physics of aerosol and photochemical smog formation in urban environments using a unique combination of absorption spectroscopy and mass spectrometry.

Proton transfer reaction mass spectrometry (PTR-MS) is already an established technique for the sensitive detection of many gas-phase OVOCs [1]. A schematic diagram of the PTR mass spectrometer developed at Leicester University is shown in **Figure 4**. However, PTR-MS is unable to distinguish between molecules of the same mass, leading to potentially ambiguous detection of certain atmospheric species. By utilising PTR-MS together with broadband cavity enhanced absorption spectroscopy (an ultra-sensitive type of optical absorption spectroscopy [2], which is highly specific to OVOCs such as glyoxal), we are studying the complex array of gaseous organic oxidation products that lead to SOA production. The aim of our research is to elucidate underlying chemical degradation mechanisms leading to OVOCs and hence identify potential species contributing to incipient aerosol formation and growth in the urban atmosphere.

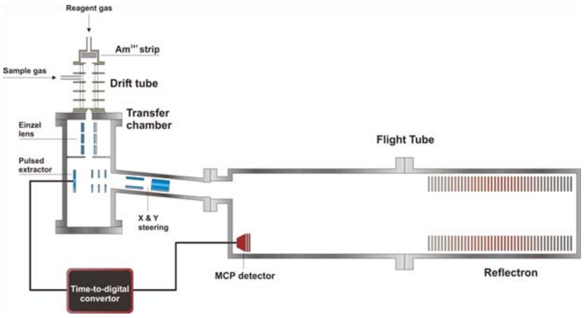

Figure 4: *Schematic of the PTR-ToF mass spectrometer. Ambient air is sampled continuously into the instrument. VOC molecules are protonated by reaction with hydronium reagent ions (H_3O^+) and are detected as $(VOC–H)^+$ molecular ions using time of flight mass spectrometry. Diagram courtesy of Dr K. Wyche, Leicester University.*

[1] R. S. Blake, P. S. Monks and A. M. Ellis, *Chem. Rev.*, 2009, **109**, 861.

[2] S. M. Ball and R. L. Jones, Chapter 3 of *Cavity Ringdown Spectroscopy: Techniques and Applications* (edited G. Berden & R. Engeln), Blackwell Publishing, 2009.

6. Constraining the budgets of hydrogen and carbon monoxide through *in situ* measurements and modelling

Aoife Grant, Alexander T. Archibald, Simon O'Doherty, and Dudley E Shallcross

School of Chemistry, University of Bristol

Hydrogen (H_2) is the second most abundant atmospheric trace gas. It acts as an indirect greenhouse gas by removing the hydroxyl radical and thus increasing the lifetimes of other greenhouse gases. Recent increased interest in H_2 is due to its possible introduction as a "clean energy" alternative fuel. However, its current atmospheric budget is poorly constrained, particularly its source from primary and secondary emissions. Carbon monoxide (CO) is central in controlling the abundance and distribution of the hydroxyl radical. The secondary production of CO from the oxidation of volatile organic compounds (VOCs) remains the most poorly constrained sector of its global budget.

Figure 5: *The instrument developed at Bristol University for high-frequency measurements of ambient H_2 and CO concentrations.*

This study investigates the primary and secondary production of H_2 and CO using a combination of in-situ measurements and modelling. High-frequency measurements of H_2 and CO at an urban location provide detailed information on concentration time-series, diurnal cycles, and the sources and sinks of H_2 and CO. These urban measurements help to improve assessments of primary anthropogenic emissions of H_2, largely from transport. Modelling of the secondary production of H_2 and CO was carried out using a box model to produce individual conversion factors of VOC oxidation to H_2 and CO yields. To maintain the oxidation balance within global chemical transport models (which typically do not include a detailed suite of VOCs reactions), it may be vital to include the H_2 and CO produced from VOC oxidation reactions.

7. Trace metal contamination of lakes and ponds in London

C. J. Hall, N. L. Rose, and A. W. Mackay

Environmental Change Research Centre, University College London

London has a long history as an urban and industrial centre, and air pollution has been a concern since the 17th century. Trace metals are one type of air pollutant that at certain concentrations can be harmful to organisms, including humans. Historic levels of metal contamination within the city are being determined by analysis of sediment cores from seven lakes. **Figure 6** shows the results of the analysis of a core from Wake Valley Pond in north east London. The concentration profiles of each metal are similar. For example, Pb shows a steep rise occurring in the early 1900s, to peak values of 423.7 µg/g during the 1950s, before declining towards the present day. This reflects the impact of the Industrial Revolution and the instigation of the Clean Air Act in 1956. Metals stored in sediments can be reintroduced into the aquatic ecosystem and become potentially harmful to biota.

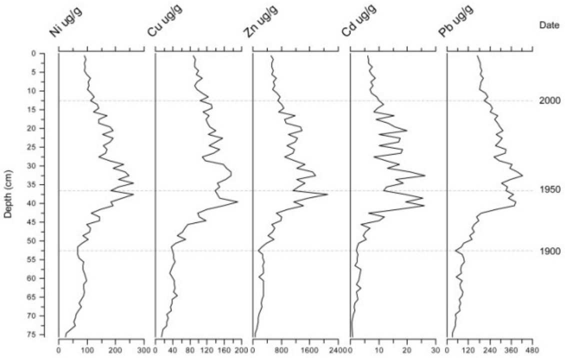

Figure 6: *Metal concentrations (µg/g) in a core taken from Wake Valley Pond.*

Metal concentrations are also being determined in sediment, water, atmospheric deposition and a range of biota at the Vale of Health Pond (north central London) over the course of one year. The historic and contemporary datasets will then be combined to assess the potential toxicity of metals in London's lakes.

8. CityScan: the scanning imaging DOAS system

R. Graves[1], R. Leigh[2], C. Whyte[2], and P. S. Monks[1]

1. Department of Chemistry, University of Leicester

2. Department of Physics and Astronomy, University of Leicester

Air quality is an international issue and the subject of several European directives [1] on pollution levels because, at high concentrations, atmospheric pollutants can have significant effects on human health, ecosystems and the climate. The main sources of air pollutants such as NO_x (NO_2 and NO), CO, volatile organic compounds and particulate matter in the UK are motor vehicles and power generation [2]. It is becoming increasingly important to measure changes in these air pollutants, particularly in urban environments where these pollutants can be present at highly elevated levels.

A scanning imaging differential optical absorption spectroscopy (DOAS) system called *CityScan* has been developed at the University of Leicester. CityScan will be used to monitor air quality in urban areas by measuring (i) NO_2 concentrations [3], and (ii) the oxygen dimer absorption signal which provides an indicator of aerosol optical depth [4]. This instrument will be deployed to study air quality in several urban areas, including Leicester and London and at a variety of point sources. CityScan will have significant advantages over currently available technologies [5] and will produce near real-time, three-dimensional maps of NO_2 over entire urban areas, providing unprecedentedly detailed information on air quality.

[1] Directive 2008/50/EC of the European Parliament and Council on ambient air quality and cleaner air for Europe.

[2] AEA Technology for DEFRA, Air Pollution in the UK 2009 (2010).

[3] Kramer, L. *et al.*, *Journal of Geophysical Research*, 2008, **113**, D16S39.

[4] Wagner, T. *et al.*, *Journal of Geophysical Research*, 2004, **109**, D22205.

[5] Whyte, C. *et al.*, *Atmospheric Measurement Techniques*, 2009, **2**, 789-800.

9. A new method to investigate regional scale carbon budgets from satellite measured CO_2

A. J. Hewitt[1], H. Boesch[1], M. P. Barkley[2], C. Witham[3], A. Manning[3], and P. S. Monks[4]

1. EOS, Department of Physics & Astronomy, University of Leicester

2. Institute of Atmospheric and Environmental Science, University of Edinburgh

3. U.K. Met Office, Exeter

4. Department of Chemistry, University of Leicester

Atmospheric CO_2 concentrations have been retrieved from measurements made in the near infrared by the SCIAMACHY instrument, using the Full Spectral Initiation (FSI) WFM-DOAS algorithm. A methodology has been developed to investigate regional scale carbon budgets, by coupling the UK Met Office's NAME dispersion model with satellite measured CO_2 and top-down / bottom-up carbon flux models.

The method was used in forward mode, where top-down surface flux information from CarbonTracker was combined with the background CO_2 mixing ratio to obtain an atmospheric concentration. Synthetic testing of the initialisation method demonstrated that a strong correlation coefficient ($R^2 \approx 0.9$) between the forward modelled and satellite observed atmospheric CO_2 fields can be achieved.

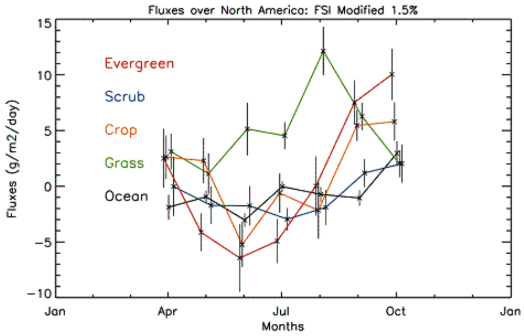

Figure 7: *Flux magnitudes from the inversion of FSI-WFM-DOAS retrieved SCIAMACHY CO_2 concentrations.*

The model was also run in inverse mode, where the change in carbon mass between the satellite-retrieved concentration and the background concentration was combined with the residence times from the NAME model. With the assumption that the region investigated consists of homogeneous carbon flux ecoregions, flux values (e.g. **Figure 7**) were assigned to the ecoregions which provide the best match with the observed mass exchange between foreground and background satellite measurements. On the regional scale, this method could improve on the carbon flux estimates from CarbonTracker and an equivalent Eulerian method.

10. A study of Martian atmospheric chemistry through laboratory and computer-based simulation

Maria K. D. Duffy, Stephen R. Lewis, and Nigel J. Mason

Department of Physics and Astronomy, The Open University

The observation of a methane plume in the atmosphere of Mars caused much interest in the role of trace gases in the Martian system [1]. Investigating the way that trace species such as ozone, water and HCl are cycled in the atmosphere will give insight into the interactions taking place between the atmosphere, lithosphere and any potential biosphere of the Red Planet. Current Mars General Circulations Models (MGCMs) with coupled chemistry modules focus on odd-hydrogen (HO_x) and odd-oxygen (O_x) chemistry and so are not yet capable of simulating more complex chemical interactions.

In the current project, a Mars environmental simulation chamber containing a Mars-like gas mixture with added trace gases will be irradiated by a solar simulator. The effect of the addition of a Mars-analogue regolith on the reaction mechanisms and rates will be investigated. The reactions identified in the laboratory will then be added to the chemical module of the Laboratoire de Météorologie Dynamique (LMD)-MGCM [2], [3]. Numerical experiments will be conducted to identify sources of trace species on the surface, by conducting trial releases and observing the species' distribution after a set period of time. The interaction of the current chemical module with new reactions as determined by the laboratory simulations will also be investigated.

[1] Mumma, M. J. *et al.*, *Science*, 2009, **323**, 1041-1045.

[2] Forget, F. *et al.*, *J. Geophys. Res. (Planets)*, 1999, **104**, 24155-24175.

[3] Lefèvre, F. *et al.*, *J. Geophys. Res. (Planets)*, 2004, **109**, E07004.

Abstracts provided by Forum delegates: edited by **STEPHEN BALL** and **BILL BLOSS**

The ECG plans to hold the next Atmospheric and Environmental Chemistry Forum in winter 2011/spring 2012.

Forthcoming Symposium

The Nitrogen Cycle—in a fix?

RSC Environmental Chemistry Group 2011 Distinguished Guest Lecture and Symposium

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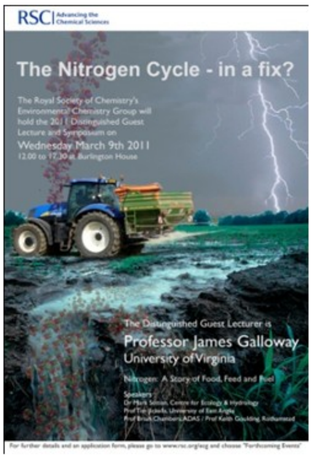
A one-day symposium organised by the RSC's **Environmental Chemistry Group** (ECG) and the **Environment, Sustainability and Energy Division of the Royal Society of Chemistry**, incorporating the **2011 ECG Distinguished Guest Lecture** to be given by **Prof. James Galloway** (University of Virginia).



RSC | Advancing the Chemical Sciences

The Nitrogen Cycle - in a fix?

The Royal Society of Chemistry's Environmental Chemistry Group will hold the 2011 Distinguished Guest Lecture and Symposium on

Wednesday March 9th 2011

12.00 to 17.30 at Burlington House

The Distinguished Guest Lecturer is

Professor James Galloway

University of Virginia

Nitrogen: A Story of Food, Feed and Fuel

Speakers

Dr Mark Sutton, Centre for Ecology & Hydrology

Prof Tim Jickells, University of East Anglia

Prof Brian Chambers, ADAS / Prof Keith Goulding, Rothamsted

For further details and an application form, please go to www.rsc.org/ecg and choose "Forthcoming Events"

Where: The Royal Society of Chemistry, Burlington House, Piccadilly, London

(The nearest tube stations are Green Park and Piccadilly Circus)

When: Wednesday 9th March 2011

PROGRAMME

12.00 Buffet lunch, coffee

13.00 Dr Mark Sutton, Centre for Ecology & Hydrology, Edinburgh, *The atmospheric nitrogen cycle and climate*

13.45 Prof Tim Jickells, University of East Anglia, *Atmospheric nitrogen inputs to the marine environment*

14.30 Tea/coffee; **Thirty-eighth ECG Annual General Meeting**

15.00 Prof Brian Chambers, ADAS consultants/Prof Keith Goulding, Rothamsted, *Optimising nitrogen use efficiency in agriculture*

15.45 Introduction to the ECG Distinguished Guest Lecture for 2011 and presentation of the ECG DGL medal

15.50 2011 ECG DGL: Prof James Galloway, University of Virginia, *Nitrogen: a story of food, feed and fuel*

16.50 General Discussion

17.15 Close

For further details, please see **www.rsc.org/ecg** and choose "Forthcoming Events"

RSC ENVIRONMENTAL CHEMISTRY GROUP

The Nitrogen Cycle – in a fix?

Admission is by ticket only. In order to register for this meeting, please complete the slip below and return to Dr William Bloss by email, post, or fax (see details below). There is a charge of £25 for members of the ECG and £50 for non-members of the ECG (£25 concessions, i.e. student/unwaged; proof required). Cheques should be returned with this form (made payable to *RSC Environmental Chemistry Group*). **Early application is encouraged as places are limited and will be allocated on a first come first served basis. Five places are reserved free for retired members; these will also be allocated on a first come first served basis.**

Name: ………………………………………………………………………………………………

Affiliation: ……………………………………………………………………………………

Address: ………………………………………………………………………………………

Email address: ………………………………………………………………………………

I would like to attend: **The Nitrogen Cycle – in a fix? Symposium** ☐

The ECG AGM ☐

I enclose a cheque for:

☐ **£50 (non-member)**

☐ **£25 (ECG members/non-ECG concessions: RSC membership no: ……………**

☐ **I would like to attend as a retired RSC and ECG member**

Dietary/access requirements…………………………………………………………………………………………

Signed: ………………………………………………………………………………………

Date: …………………………………………………………………………………………

Please return to: Dr William Bloss, School of Geography, Earth & Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT

Tel.: 0121 414 2558 Fax: 0121 414 3709 Email: w.j.bloss@bham.ac.uk

Meeting report

Contaminated land: chemistry and toxicology aspects of chemical risk assessment

"Exploring the science applied in models used to assess the risk to long-term human health from contaminants in soil"

This one-day meeting, organised jointly by the RSC Environmental Chemistry Group and the RSC Toxicology Group took place in the Chemistry Centre at Burlington House, Piccadilly on 28th September, 2010.

The meeting was aimed at practitioners involved in assessing and remediating contaminated land, and focused on risk assessment models used to estimate chronic exposure from **oral**, **inhalation** and **dermal** pathways. Forty-three delegates attended from a wide range of organisations including consultancy firms, regulatory authorities, and academia.

Dr Sohel Saikat (Health Protection Agency) opened the proceedings with a presentation entitled *Oral bioaccessibility data: missing the point in exposure assessment of soil-borne chemicals*. He introduced the concepts of contaminant bioavailability and bioaccessibility and described methods of measurement and applications of data used for contaminated land risk assessment models. Using metal exposure as an example, the analysed total metal concentration in soil does not take into consideration metal speciation, which determines bioavailability and bioaccessibility. Hence total metal concentration ≥ acid extractable ≥ bioaccessible ≥ bioavailable metal concentration.

In contaminated land risk assessment, there is a general conservative assumption that a contaminant is 100% bioavailable following exposure from soil. Exposure models such as CLEA (Contaminated Land Exposure Assessment Model), which can take into account the bioaccessibility of a contaminant, provide a better method for assessing the risks to human health from exposure to contaminated land.

Dr Chris Collins' (University of Reading) presentation, *Modelling plant uptake of organic chemicals – current status and future needs*, also discussed CLEA and, in particular, the role that the uptake of organic contaminants by plants has in this model. Routes of transport for organic compounds in different types of plants were discussed and the influence that chemical properties (lipophilicity) has on cellular transport mechanisms described.

Plant uptake models used to predict the uptake of non-ionic chemicals in soil were compared. These range from simple regression models (Travis and Arms) to mechanistic (Trapp and Matthies) and fugacity models (Hung and Mackay). The more complex models tend to require a significant amount of data which are unlikely to be measured by those engaged in contaminated land risk assessment. These models are more sensitive to data variation.

Continuing the theme of the uptake of chemicals by plants, **Alan Dowding** (Food Standards Agency) reviewed *The Food Standards Agency's approach to assessing uptake of chemicals by crops from contaminated soil*. He discussed sampling and analysis of chemicals in soil and crops, including allotments, as part of the regulatory role of the FSA.

Dowding also described the PRISM model, which is used by the FSA to predict *inter alia* uptake by plants of inorganic chemicals in soil. The PRISM model incorporates data for 42 inorganic contaminants and 129 radionuclides, and uptake by plants is modelled for various transport mechanisms including deposition (wet and dry), absorption, translocations (in xylem and phloem) and root uptake.

The FSA are planning to determine levels of total and inorganic arsenic in fruit and vegetables grown in the UK and to investigate the relationship between arsenic levels in soil and crops, and the extent to which arsenic is taken up by different crop types. The focus will be on soil samples from locations with high arsenic levels of geochemical, mining or industrial origin.

Katy Baker (Arcadis) in her talk *Vapour Intrusion in the UK – Where do we go next?* described how vapour migration from the contamination of soil by volatile organic compounds (VOCs) is measured and then modelled for CLEA and other exposure models. Inhalation of vapours from volatile organic compounds in soil can be a significant exposure pathway. Exposure to VOCs is assessed by analysing soil and groundwater samples.

The Johnson and Ettinger Vapour Intrusion Model has been incorporated into CLEA. Other models used to estimate vapour intrusion, if the site of interest does not match the generic CLEA model, include CSOIL, VOLASOIL and Biovapour.

In exposure models, all VOCs have traditionally been assessed in the same way irrespective of the different physico-chemical properties of VOCs and how these may affect their environmental impact. This was illustrated with two case studies: (i) a petrol filling station (petroleum hydrocarbons); and (ii) an active industrial estate (chlorinated solvents in the subsurface). When the measured soil vapour concentrations were compared with modelled concentrations, the model tended to over predict the petroleum hydrocarbon concentrations and under predict the chlorinated solvent concentration, highlighting the variation and influence of contaminant properties.

Inhalation as an exposure route continued with a talk by **Camilla Pease** (Environment Agency) entitled *Adverse lung effects and the derivation of inhalation Health Criteria Values (HCVs)*. Lung toxicology was illustrated with examples from chronic tobacco smoking, occupational exposure (coal mining) and asbestos exposure. The UK risk assessment framework for deriving a HCV is detailed in the Environment Agency guidance document SR2. HCVs may be estimated from *in vivo* inhalation and dermal studies or from epidemiological data.

Simon Firth (Firth Consultants) (*Chemical exposure via inhalation of soil derived dust – modelling versus measurement*) explained how the inhalation of soil-derived dusts and their contaminants can be measured, what models are adopted by CLEA, and for which contaminants does the inhalation of dust become significant in terms of affecting the Generic Assessment Criteria (GAC) derivation.

The CLEA model algorithm is used to estimate chronic exposure from outdoor and indoor dust. A parameter in CLEA is used to estimate the proportion of indoor soil derived dust i.e. the Transport Factor which is default at 0.5 in CLEA and indicates that 50% of the PM_{10} particulates in dust are derived from soil. Firth has derived a value of 0.8 for the Transport Factor from his experiments, which is larger than the CLEA default value. Hence the Transport Factor can vary significantly from site to site and from contaminant to contaminant.

The last two presentations concerned the dermal route of exposure. **Alison Mckay** (Mckay Environmental Ltd) (*The dermal pathway - A touchy subject!*) reviewed the dermal exposure pathway, the available data, and uncertainties in the contaminated land risk assessment framework. Estimating dermal exposure to soil is complex, and assumptions are usually made about human behaviour to establish what the frequency and duration of exposure is, and the type of human activities that could lead to exposure to soil. Other considerations are the properties of the skin, the soil, and the contaminants. The skin acts as a living barrier, and uncertainties in estimating dermal exposure include variability in the barrier function. The CLEA model has adopted the Dermal Absorption Fraction value, derived from experimental data for each contaminant. Currently, there is a lack of experimental data on skin absorption; as more data become available, and uncertainties diminish for other exposure pathways, the relative contribution of the dermal pathway will become more important.

A presentation from **Tayo Adedeji** (Atkins) on *Dermal Exposures to soil: metabolism, toxicity and acute duration exposures* provided further information on the dermal uptake pathway and the toxic effects of dermal absorption. Effects from dermal exposure may be local or systemic, reversible or non-reversible. Local effects include irritation and defatting by solvents and systemic effects include sensitisation (nickel) and carcinogenesis (benzo[*a*]pyrene).

The meeting concluded with a question and answer session with the eight speakers as the panel and Simon Firth chair. Given the positive response to this event and to September 2009's *Contaminant Transport and Fate* meeting, the ECG would welcome ideas for topics for a third contaminated land forum, again with a chemistry focus, for 2011/2012. Please email James Lymer *via* the ECG website with your suggestions: www.rsc.org/Membership/Networking/InterestGroups/Environmental/committee.asp

Copies of the speakers' presentations from this meeting are available on the ECG website www.rsc.org/ecg.

JAMES LYMER

Contaminated Land Representative,

ECG Committee

Meeting report

Geochemical speciation & bioavailability of trace elements (GeoSpec2010)

A two-day conference on the *Geochemical Speciation & Bioavailability of Trace Elements*, organized by the Environmental Mineralogy Group (a special interest group of the Mineralogical Society) and the RSC Environmental Chemistry Group (ECG), took place at Lancaster University on 7th–8th September 2010. The meeting brought together aquatic chemists, geochemists, mineralogists, and environmental scientists and engineers to discuss recent developments in analytical and modelling methods for understanding the kinetic behaviour of trace elements in aquatic and terrestrial environments.

The **first session** (out of six for the meeting), with Dr **Imad Ahmed** (Lancaster University) in the chair, started appropriately with a plenary lecture by Prof. **Bill Davison** (Lancaster University) on developments in chemical speciation and bioavailability. Progress in speciation measurements in natural waters over the last 50 years was reviewed and areas which would benefit from further research were highlighted.

The **second session**, chaired by Dr **Simon Nelms** (Thermo Fisher Scientific), began with a paper by Dr **Scott Young** (Nottingham University) on the use of isotopic dilution techniques to determine the reactive pool of trace elements in soils. Soils are spiked with a radioactive tracer or a natural isotope and the E-value (isotopically exchangeable pool of an element) is measured following equilibration. Results from the isotopic exchangeability of Pb and the lability of As and Se in different types of soils illustrate this technique. The session continued with an account by Dr **Raimund Wahlen** (Agilent UK Ltd) of developments in ICP-MS instrumentation for determining elemental and organic species in the environment. Applications included arsenic speciation by LC-ICP-MS and the use of GC-ICP-MS for separating and quantifying organotin compounds in the marine environment.

Dr **Dmitrii Kulik** (Paul Scherrer Institute) opened the **third session** (chaired by Prof. **Ed Tipping** from the Centre of Ecology and Hydrology, Lancaster) with a paper on "Thermodynamic modelling of solid-aqueous geochemical speciation". The Gibbs Energy Minimization (GEM) method was used to calculate chemical equilibria of surface complexes at mineral-water interfaces. These computations permit the whole continuum of aqueous speciation–heterogeneous adsorption–surface co-precipitation–solid solution to be modelled. GEM modelling has been used to investigate e.g. the solubility of kaolinite; aqueous speciation of radionuclides [Am(III), U(IV), U(VI), and Eu(III)]; and surface complexation of Eu(III) on Na-montmorillonite. (Software used for GEM was explained at the close of this session *vide infra*).

Prof**. Erik Smolders** (Katholieke Universiteit Leuven, Belgium) continued this session with a presentation on "The role of speciation on trace metals availability to higher plants". Free metal ion activities in soils poorly describe metal uptake by plants. By applying the technique DGT (Diffusive Gradients in Thin-films) to soil analysis, a better correlation was found between soil and plant metal ion concentrations (Smolders *et al.*, *Environ. Toxicol. Chem.*, 2009, **28**, 1633-1642).

The first day of the conference ended with a short training course led by Dr **Dmitrii Kulik** on the Gibbs Energy Minimization software package (GEMS) (http://gems.web.psi.ch). This method for the thermodynamic modelling of heterogeneous aquatic geochemical systems can be applied *inter alia* to studying metastable and dispersed mineral phases, solid solution–aqueous solution equilibria, and adsorption/ion exchange systems.

The second day of the conference, chaired by Prof. **Bill Davison**, opened with a paper by Prof. **Stan van den Berg** (University of Liverpool) on "Speciation of iron and copper, and evidence for metal competition in the marine system". Humic substances (HS) bind with Fe in seawater; Fe-HS species are widespread in coastal waters and deep ocean (at low levels). Competition occurs between Cu and Fe for HS complexation in natural samples. The labilities of the various metal complexes of HS were studied using anodic and cathodic stripping voltammetry.

Prof. **Willem van Riemsdijk** (Wageningen University, Netherlands) continued this **fourth session** by describing the use of the Donnan Membrane Technique (DMT) for *in situ* measurements of "free metal" ion concentrations in the presence of inorganic and organic complexing agents. For example, free Al^{3+} ion concentrations at a level of 10^{-9} M have been determined in humic acid solutions. More recently, anion-DMT, which uses an appropriate anion-exchange membrane, has been developed to study the transport and speciation of Cl^- and SeO_4^{2-} ions.

Further aspects of DGT (Diffusive Gradients in Thin-films) technology were discussed in the **fifth session**, chaired by Dr **John Hamilton-Taylor** (Lancaster University). In DGT, analytes diffuse across a layer of defined thickness (a polyacrylamide hydrogel covered with a protective membrane). Diffusion is followed by binding to, typically, Chelex-100 resin located within the hydrogel. DGT selectively accumulates free metal cations, simple inorganic complexes and the labile metal-organic matter complexes. Dr **Hao Zhang** (Lancaster University) in her talk ("Dynamic aspects of speciation and bioavailability of trace metals in waters and soils: challenges and rewards from measurements using DGT") explained that DGT is an *in situ* time-integrated technique which requires sufficient deployment time to accumulate or equilibrate the analytes to enable their measurement. Dr Zhang pointed out that results from DGT are in agreement with the concentration of nutrients (e.g. phosphorus) in plants, which validates using DGT to determine metal uptake dynamics in plants.

Prof. **Herman Van Leeuwen** (Wageningen University, Netherlands) spoke on "Physicochemical aspects of the DGT behaviour of nanoparticulate and colloidal species". Herman's team have shown that humic and fulvic acids can penetrate and accumulate in the hydrogels used for DGT and DET (Diffusive Equilibrium in Thin-films) devices. Accumulation of humic acid and metals is at its highest in media of relatively low ionic strength. This is a consideration for determining metal ion levels by DGT in, for example, freshwater samples. (*Environ. Sci. Technol.*, 2010, **44**, 4253-4257; 5523-5527).

[Applications of DGT in environmental analysis were the topic for Bill Davison's ECG DGL in 2003 – see ECG Bulletin *July 2003 pp 3-4].*

The **sixth and final session** of this conference (chaired by Dr **Joe Small**, National Nuclear Laboratory) began with a paper by Prof. **Jon Gustafson** (Royal Institute of Technology, Sweden) "Lead sorption to soils: a challenge for modellers". Prof Gustafson has studied Pb^{2+} adsorption on ferrihydrite ($Fe_2O_3{\cdot}H_2O$) at various pH and anionic species concentrations. He showed that Pb binding to Fe oxyhydroxides and organic matter are stronger than previously realised, and that the Pb^{2+} binding-site affinity on ferrihydrite is heterogeneous. His findings suggested that both Fe-oxyhydroxides and organic matter bind Pb^{2+} more strongly under environmental conditions. This may be due to the existence of high-affinity site for Pb, which does not sorb other cations, and explains the poor performance of many geochemical models for Pb adsorption.

Dr Steve Lofts (Lancaster) closed the session with a paper on "Testing the WHAM model: comparison of field measurements of free metal ion concentrations with model predictions". Windermere Humic Aqueous Model (WHAM) is a discrete site/electrostatic model describing metal and proton interactions with humic substances. WHAM contains a large database of metal-HA/FA binding constants incorporating over 30 metals and radionuclides. Discrepancies between observed and predicted metal ion concentrations using WHAM are thought to be due to uncertainties and /or bias in the measurement of free ion activities.

Poster session. In conjunction with the twelve keynote lectures there was a poster session for PhD students and early career postdoctoral workers. Six out of the 33 posters which featured at the meeting have been expanded by their authors into papers for the ECG *Bulletin*. An extended summary of these six papers appears on pp 5–16 of this issue and the complete (partly edited) papers accompany the web version of the January 2011 ECG *Bulletin* (www.rsc.org/ecg and links).

Before closing the conference, Prof. **Jamie Lead** (Editor, *Environmental Chemistry*, CSIRO, Victoria, Australia) awarded prizes for the best posters to **Ezzat Marzouk** (PhD student, Nottingham University) and **Jacqui Levey** (Lancaster University).

Dr IMAD A. M. AHMED
(Conference Co-organizer)

Lancaster Environment Centre
The University of Lancaster
December 2010

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Meeting report

RSC General Assembly 2010

The RSC General Assembly functions as an advisory body to Council. Its role is to advise on the strategy, policy and activities of the RSC, enabling the views of members to be represented, and to facilitate communication and coherence within governance and the chemical science community. The RSC General Assembly comprises Council Members and representatives of the Local Sections and the Interest Groups. Representatives of some committees and other groupings may also be involved. The sixth RSC General Assembly was held in Birmingham during 12th–13th November 2010.

The General Assembly began with talks by **Peter Cook** (Past Sheriff of the City of London) and Professor **David Clary** (Chief Scientific Advisor to The Foreign and Commonwealth office) who spoke on “Future Role that Chemistry Can Play in Keeping the UK Competitive” and “A Chemist in the Foreign Office”, respectively.

This was followed by parallel track sessions, and I attended the “Tackling roadmap challenges” discussion which enumerated the top ten challenges out of forty-one in the RSC roadmap:

1. Agricultural Productivity
2. Conservation of scarce natural resources
3. Conversion of biomass feedstocks
4. Diagnostics for human health
5. Drinking water quality
6. Drugs and therapies
7. Energy conversion and storage
8. Nuclear energy
9. Solar energy
10. Sustainable product design.

(http://www.rsc.org/scienceandtechnology/roadmap/index.asp)

These themes continue to be a productive source of ideas for new RSC conferences, publications and workshops.

“Demonstrating the value of chemistry research to policy makers” was the next item when the assembly discussions resumed. The RSC has tried to engage policy makers with publications such as *Finances of Chemistry and Physics Departments in UK Universities* (June 2010) and *The Economic Benefits of Chemistry Research to the UK* (September 2010) (www.rsc.org/policy). *MyRSC* is seen as a key tool for consulting with the wider RSC membership. The RSC is also working hard to ensure that its parliamentary links expand and its influence in Europe and internationally increases.

RSC Interest Groups and their *modi operandi* was the topic for discussion at the start of the second day. **Richard Allen** from the Water Science Forum (WSF) explained how WSF has evolved a ‘best practice’ for organising its conferences. An idea/concept for a conference is presented to the WSF Committee which, if it agrees to take the idea further, appoints a lead committee member to create a business case and an agenda for the event. This is then resubmitted to the Committee. A template, which will soon be available on *MyRSC*, has been produced to facilitate these various stages. If the Committee agrees that the conference should proceed then, for individual contracts with >£5K liability, RSC approval is sought, and arrangements made for attendance to be counted towards individual CPD targets. A working group of an appropriate size and expertise is then set up. Establishing financial liability between co-sponsors/organisers is essential. A risk assessment for the conference venue and activities is also mandatory. After the conference, a review takes place and the financial aspects audited as part of the annual accounts procedures.

The next presentation was by a representative of the RSC Marketing Interest Group, which was formed in 1995 and now has over 300 members. The group provides a focal point within the RSC for members to discuss, exchange ideas and learn about the marketing of chemicals, chemicals-based products and technology. It also helps members with other factors which influence the marketing of chemicals, such as environmental issues and changes in health and safety legislation.

Group meetings are arranged 12 months in advance to start usually at 6.30 pm in Burlington House.

Recent topics include *What exactly is a Business Strategy?*; *The chemistry and marketing of chocolate*; and *New marketing tools for scientific instrumentation in the laboratory*. Committee meetings are held at 4.00 pm on the same day. A meeting organised near Christmas for presentations by post-graduate students is an opportunity for employers and potential employees to meet and mingle.

Fiona McMillan, who is the RSC Member Networks Specialist with a responsibility for Interest Groups, explained in some detail how Interest Groups should liaise with the RSC and manage their activities:

- She requested that Honorary Secretaries of Interest Groups provide her with copies of meeting minutes and keep her informed of committee membership changes.

- Fiona can supply on request information concerning the geographical distribution of Interest Group members and also their job categories.

- The data-protection checklist is now distributed by the Membership Department and will need to be completed and returned by each committee annually.

- Fiona also offered some clarification concerning Interest Group membership and membership of the RSC. Members of Interest Groups have to be members of the RSC (or affiliate members) unless they have membership of some other (more appropriate) body (e.g. librarians may well be members of their own chartered body and this would be seen as entirely appropriate); non-members can also be co-opted to Interest Group committees. However, Charity Commission regulations require that committee post holders (Chair, Vice-Chair, Honorary Secretary, Honorary Treasurer) are members (or affiliate members) of the RSC.

Kathryn Westmore and **Linden Smith** talked about the role of the RSC as a charity. RSC fundraising activities throughout 2006-2009 raised £4m for short-term educational/international goals and currently there is a development campaign targeting the accumulation of legacies and trusts *via* links with the chemical industry, government, individuals, and charities. Priority areas for development are science and education, public engagement through Chemistry Centre activities, the President's Fund (which, for example, promotes 3rd world education) and the Benevolent Fund. Individuals (such as the members of the Interest Groups) contribute significantly by giving their time.

The development goals are fundamentally focused on the RSC aim: *To be foremost in the world in promoting and developing the Chemical Sciences for the benefit of society* by:

- enhancing collaboration between government, academia, industry and communities (e.g. Pan Africa Chemistry Network, Chemistry Leadership Network in India)

- raising awareness of the value of the chemical sciences (e.g. £1m from the Wolfson Foundations to refurbish the Chemistry Centre)

- the 'Burlington House' Public Lecture series

- working with Interest Groups to identify opportunities for networking and development.

The assembly closed with the Presidential Address by Professor **David Phillips** OBE who sketched out the RSC's various international activities (e.g. representation at EuCheMS, the RSC office in Shanghai, the UK-Malaysia Symposium on Medicinal Chemistry 2008, the Pan Africa Network), publishing ventures (e.g. the new flagship journals *Chemical Sciences* and *MedChemComm*; books such as the drug discovery series) and products such as ChemWord, Discover LabSkills and ChemSpider.

What is apparent from my attendance at the Assembly is that the RSC has a reinvigorated dynamic focused on education, media presence, internationalisation, links with government, and networking with industry; and there is a great deal of evidence of progress and much optimism about more to come.

Dr LEO SALTER

Chair, ECG Committee

Book review

Atmospheric Chemistry

Ann M. Holloway and Richard P. Wayne

Royal Society of Chemistry, Cambridge, UK, 2010, xiii + 271 pp, ISBN 978-1-84755-807-7, £25.99 (hardcover)

Ann Holloway and Richard Wayne's new text *Atmospheric Chemistry* follows on from Wayne's definitive *Chemistry of Atmospheres* (3rd edn., Oxford University Press, 2000), an authoritative book familiar to generations of graduate students, researchers and practitioners in atmospheric science. *Atmospheric Chemistry* covers much of the material from the earlier books, but with updated content, and somewhat less chemical and physical detail – the book is substantially shorter than its 775 page predecessor – with an intended audience of undergraduate or (early) postgraduate students. An integrated approach is taken to key topics in terms of their impacts, for example atmospheric ozone, and climate change.

The book starts with fairly standard chapters on the general composition of the atmosphere, its physical structure (temperature and large-scale dynamics) and an overview of the sources and sinks of atmospheric constituents on a global scale. Simple examples place the budget data in context – for example, that the human population of the UK emits of the order of 10^9 litres of methane per year... The approaches used to study atmospheric chemistry (observations and models), followed by brief accounts of the general chemistry of atmospheric ozone (with tropospheric and stratospheric behaviour considered together), the principal atmospheric cycles by chemical family (sulphur, carbon, nitrogen *etc.*) and the influence of life upon the contemporary and palaeo– atmospheric composition.

The real meat of the book comes in the final chapters, covering the chemistry of the troposphere, the stratosphere, and man's adverse influences on the atmosphere, which ranges from "classical" issues such as acid rain and ground level ozone production through to climate change. Much of the material here is drawn from the latest (2007) assessment of the Intergovernmental Panel on Climate Change (IPCC), so broadly reflects our current understanding. This section focuses upon the physical drivers of climate change, but includes some discussion of likely impacts and the ongoing political and legislative debates, concluding with the Copenhagen summit of late 2009; the integrated approach helps the reader understand both the issues of basic science and practical implementation that must lie behind future climate negotiations.

Compared with *Chemistry of Atmospheres*, the book includes many more figures, including colour, and is in general more attractive and much more accessible to the lay reader, but retains the engaging and elegant writing style. The cost for the reduced length is of course the loss of quantitative detail for certain topics of interest to those pursuing the subject in depth, for example ozone photochemistry and (aspects of) planetary atmospheres, but the extent of coverage is judged well for the target audience. Overall the book is likely to find wide use by undergraduates and those embarking upon postgraduate study in relevant fields, and in providing a broader context to the air quality work performed by local authorities and other bodies.

Reviewed by **Dr W. Bloss**, University of Birmingham

News of the Environment, Sustainability and Energy Division

The former Environment, Sustainability and Energy Forum (ESEF) has been given Divisional status within the Royal Society of Chemistry and been renamed the **Environment, Sustainability and Energy Division** (ESED), reflecting the importance of these three strands of interdisciplinary science for future RSC policy and initiatives.

ESED is committed to pushing forward the RSC's Roadmap activities and has identified three priority topics: solar energy; home energy; air quality. It is anticipated that the Interest Groups associated with ESED will be involved in providing expertise activities which support this. This strategy will enhance coherence and communication between RSC Interest Groups and ESED.

ESED will be running several meetings and events in collaboration with the Interest Groups during 2011. These will be tailored to achieving the Roadmap goals. Activities will commence on the 16th February, at Burlington House with a workshop on Air Quality. Presenters have been chosen to provoke discussion about issues consequent to the different perspectives on local air quality assessment from the point of view of their own area of expertise. The areas to be covered include modelling data versus monitoring data, the contribution of laboratory-based chemistry to Local Authority practice, the difficulty in finding financially pragmatic local planning solutions to meet national air quality policy standards . . . and similar. For instance, there may be many problems with modelling, but this meeting is concerned with how modelling *per se*, as an approach, integrates coherently with the other themes involved in local air quality management,

The outcome of the meeting will be the identification of issues where a higher level of connectedness between workers in the field might produce better implementation of policy.

At the first ESED committee meeting in February, the committee will be identifying themes and organising a dynamic programme of events for the year to come.

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

The following books on environmental topics and toxicology have been acquired by the Royal Society of Chemistry library, Burlington House, during 2010.

Environmental Forensics: Proceedings of the 2009 INEF Annual Conference
R. D. Morrison (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 628.5:340
Website: RSC eBook

Innovations in Fuel Cell Technologies
R. Steinberger-Wilckens (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 662:628.5

In Silico Toxicology: Principles and Applications
M. T. D. Cronin (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 615.9
Website: RSC eBook

Sustainable Solutions for Modern Economies
R. Hofer (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 628.5
Website: E-book link

Thermochemical Conversion of Biomass to Liquid Fuels and Chemicals
M. Crocker (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 662:628.5
Website: http://ebook.rsc.org/?DOI=10.1039/9781849732260

Understanding Environmental Pollution
M. K. Hill, Cambridge University Press, Cambridge, 2010
Shelf Mark: 628.52

Water System Science and Policy Interfacing
P. Quevauviller (ed.), Royal Society of Chemistry, Cambridge, 2010
Shelf Mark: 546.212
Website: RSC eBook

A new online facility now allows RSC members to search the library catalogues and save their searches. Go to http://www.rsc.org/opac for details.

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