



Bulletin



Knole House as depicted in Morris's *Seats of Noblemen and Gentlemen* (1880). The preservation of artefacts in a controlled environment in National Trust properties such as Knole House, Kent, is a challenge for curators – *The science behind our cultural heritage*, p 14.

In this issue

The science behind our cultural heritage was the topic for a meeting held jointly by the RSC's ECG and the Institute of Physics' Environmental Physics Group in October 2013. **Knole House** was one of the UK's stately homes mentioned at this meeting, and a report may be found on p 14 of this issue. Another meeting report (pp 15-16) summarises a forum held at Burlington House in September 2013 on *Environmental monitoring in the energy sector: exploring parallels between shale gas and nuclear*, organised by the RSC's Environment, Sustainability and Energy Division.

Elsewhere, **Dr Michael Priestnall**, a chemist and materials scientist with expertise in low carbon energy technologies, and the founder and CTO of Cambridge Carbon Capture, discusses how mineral carbonation may contribute to large-scale carbon dioxide sequestration (pp 9-10). And **David Megson** and **Sarah Dack** from the Biogeochemistry Research Centre, Plymouth University provide an overview of PCBs (polychlorinated biphenyls) – their analysis, risk assessment, and environmental impact in the UK (pp 4-8).

Also

A report from a meeting on *Tropospheric aerosol – formation, transformation, fate and impacts*; information on the recently adopted Minamata Convention on Mercury; details of two forthcoming symposia – *Plastic debris in the ocean* and *Organic chemistry and toxicity of contaminants in the ground*; and two new *ECG Environmental Briefs* – *Atmospheric chemistry at night* and *Atmospheric particulate matter*. These briefs continue our series of guidance notes on topics of importance in the environmental sciences.

Contents

Chairman's report for 2013	...3
'PCB analysis, risk assessment and forensic techniques	...4
Mineral carbonation and industrial CO ₂ sequestration	...9
ECG 2014 DGL & Symposium: 'Plastic debris in the ocean – a global environmental problem'...	11
Meeting report: Tropospheric aerosol – formation, transformation, fate and impacts	...12
Meeting report: The science behind our cultural heritage	...14
Meeting report: Environmental monitoring – shale gas v. Nuclear Minamata Convention on Mercury	...15
<i>ECG Environmental Briefs</i> EGEB No 3: Atmospheric chemistry at night	...18
<i>ECG Environmental Briefs</i> EGEB No 4: Atmospheric particulate matter	...21
RSC Green Chemistry Series: <i>Element Recovery and Sustainability</i>	...23
Forthcoming symposium: Organic chemistry and toxicity of contaminants in the ground	...24

The ECG *Bulletin* is printed on paper made from wood pulp sourced from sustainable forests, and is suitable for archival storage. This issue of the ECG *Bulletin* was printed by My Complete Print, Unit 5, Dinnages Business Park, 22 Wivelsfield Road, Haywards Heath, West Sussex RH16 4EQ. Tel.: 01444 456673.

ECG Bulletin

Published biannually by the Royal Society of Chemistry's (RSC) Environmental Chemistry Group (ECG), Burlington House, Piccadilly, London, W1J 0BA, UK

Editorial team

Executive editor

Julia Fahrenkamp-Uppenbrink
ecgbulletin@hotmail.co.uk

Production editors

Roger Reeve
University of Sunderland
roger.reeve@sunderland.ac.uk

Rowena Fletcher-Wood
Birmingham University
rls155@bham.ac.uk

Editorial Board

Stephen Ball, Leicester University
Jo Barnes, University of the West of England, Bristol
Bill Bloss, Birmingham University
Zoe Fleming, Leicester University
Martin King, Royal Holloway, University of London
James Lymer, Wardell Armstrong LLP, Sheffield
Rupert Purchase, Haywards Heath
Leo Salter, Cornwall
Stuart Wagland, Cranfield University

Environmental Chemistry Group

www.rsc.org/ecg

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.

Chair

Bill Bloss, University of Birmingham
w.j.bloss@bham.ac.uk

Vice-Chair

James Lymer, Wardell Armstrong LLP, Sheffield
jlymer@wardell-armstrong.com

Honorary Secretary

Martin King, Royal Holloway, University of London
m.king@es.rhul.ac.uk

Honorary Treasurer

Jo Barnes, University of the West of England, Bristol
annaaj_senrab@hotmail.com

ECG *Bulletin* © The Royal Society of Chemistry—Environmental Chemistry Group 2012
Registered Charity Number 207890

This and previous issues of the ECG *Bulletin* are available without charge online at www.rsc.org/ecg. For ECG membership details, visit www.rsc.org/Membership.

Chairman's report for 2013

During 2013, the Environmental Chemistry Group Committee organised a number of successful meetings, events and activities across a range of topics and formats, and in some cases jointly with other interest groups, and organisations. In February, the ECG, the RSC Separation Science Group and the RSC Analytical Division jointly organised an event on the **Analysis of complex environmental matrices**. This one-day meeting was attended by about 60 delegates, who heard a series of presentations from nine speakers on topics ranging from *Using comprehensive GC (GC x GC) in field devices for atmospheric chemistry* through to *Probing the water flea's biochemistry – a truly complex but high information-content environmental sample*. This was followed by the **2013 ECG Distinguished Guest Lecture and Symposium** on 20th March, on the topic of **Rare earths and other scarce metals: technologically vital but usually thrown away**. The speakers were Professor Andrea Sella (UCL; *Terra Rara – the Elemental Unknown Sea*); Mr David Merriman (Roskill Information Services; *A review of global supply of rare earths*); Dr Mike Pitts (Technology Strategy Board; *Chemistry innovation in resource efficiency*); and Dr Adrian Chapman (Oakdene Hollins; *Materials criticality – mitigation options and impacts*). The Distinguished Guest Lecture was delivered by Professor Thomas Graedel of Yale University, who spoke to the symposium title. Detailed reports from the meeting may be found in the July 2013 edition of the *ECG Bulletin*. Approximately 60 delegates from across the private, public and regulatory sectors attended the meeting.

In autumn 2013, the ECG co-organised two events with different interest groups from the Institute of Physics. On 23rd October, an evening lecture programme on **The science behind our cultural heritage**, held at the Institute of Physics, featured talks from Dr Nigel Blades (National Trust; *Heat, moisture and the preservation of art collections in historic houses*) and Mr Joseph Padfield (National Gallery; *Considering the effect of light on old master paintings*). On 20th November, the ECG and the Molecular Physics Group at the IOP co-organised a meeting on **Soft ionisation mass spectrometric techniques and the environmental sciences** at the University of Birmingham. This meeting, which followed on from the successful inaugural meeting on the same topic in November 2012, featured talks from Professor Jonathan Williams (Max Plank Institute; *The atmospheric chemistry of forests, a forgotten molecule, and a football match*); Dr Emily House (Lancaster University; *Measuring fluxes of biogenic Volatile Organic Compounds above the Amazonian Rainforest using PTR-MS*); Professor Paul Thomas (Loughborough University; *Does it have to be blood sweat and tears? Non-invasive approaches to therapeutic measurements and emergency*

medicine) and Professor Armin Wisthaler (University of Innsbruck; *An overview of on-line CIMS methods for the measurement of organic trace gases in the Earth's atmosphere*). The meeting was attended by about 55 delegates. It was agreed to hold a third meeting in the autumn of 2014, potentially to be hosted at the University of Lancaster.

The ECG has also led the development of new educational outreach materials. Committee member Dr Zoe Fleming (University of Leicester/National Centre for Atmospheric Science) secured substantial central RSC funds to develop an equipment resource for schools centred on measurements of local air quality. The project, entitled **Air Quality Monitoring and Atmospheric Chemistry in Schools**, will provide a set of monitors (currently undergoing initial trials with a group of Key Stage 3 pupils in Leicester) for use in schools with accompanying instructions, guidance, and lesson plans, and parallel online resources to allow the measurements to be accessed and used more widely by other schools.

Alongside our programme of events, three members of our Committee, Julia Fahrenkamp-Uppenbrink, Rupert Purchase and Roger Reeve have continued to produce the biannual **ECG Bulletin**. A key innovation led by Dr Martin King (Royal Holloway) has been the development of the **ECG Environmental Briefs**, a series of short documents giving a brief but precise introduction to topics of relevance to environmental chemistry. *ECG Environmental Briefs* on calculating atmospheric photolysis rates and contaminated land regulations, respectively, were published in the July 2013 edition of the *ECG Bulletin*; two more *ECG Environmental Briefs* appear in this issue. The *ECG Environmental Briefs* also have a dedicated website, which can be reached from the ECG Group website (<http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/index.asp>). The ECG appreciates suggestions for future topics and authors to develop this resource.

Forthcoming events in 2014 include **Organic chemistry and toxicity of contaminants in the ground**, a one-day meeting to be held at Burlington House on 13 February 2014, and the **2014 ECG Distinguished Guest Lecture and Symposium: Plastic debris in the ocean – a global environmental problem** to be held on 12th March 2014 at Burlington House. Full details of both events may be found elsewhere in this issue.

Dr WILLIAM BLOSS
University of Birmingham,
December 2013

PCB analysis, risk assessment and forensic techniques in UK contaminated land assessments

This article provides an overview of the current state of PCB analysis, risk assessment and forensic techniques in contaminated land assessments undertaken in the UK today. It provides a discussion on the merits and drawbacks of the current situation and provides advice on how improvements can be achieved.

Introduction

Polychlorinated biphenyls (PCBs, **Figure 1**) are a group of 209 chlorinated organic compounds that were widely used in the 20th century for a variety of industrial uses, including dielectric fluids, hydraulic fluids and plasticisers. PCBs were first produced in the 1930s and were manufactured until the 1970s and 80s, when their use was phased out because of environmental and human health risks (1, 2). PCBs are very stable compounds that do not readily degrade; they are persistent organic pollutants and are listed under the Stockholm convention as part of the “dirty dozen.” Even though the use of PCBs has been phased out, they are still routinely detected in soils and animal tissues at contaminated sites in the UK and across the globe (3, 4, 5). Findings from the UK soil and herbage survey (6) show that at the national scale, diffusive leakage from sealed and open primary sources, such as electrical equipment, is the main routes by which PCBs enter the environment.

PCBs were synthesised as blends containing a mixture of different PCBs that were sold under trade names based on their chlorine content. The market leader for PCB production was Monsanto, a US based company. It manufactured PCB mixtures called Aroclors that account for more than half of the global total of roughly 1.2 million tonnes (7). Monsanto produced nine main Aroclors that accounted for 99.97% of production (8); each was identified with a four digit code. For example, Aroclor 1260 contained an end product with 60% chlorine by weight. Similar naming systems and production methods were used by other manufacturers; the proportions of congeners in Aroclor 1260, Clophen A60 and Kanechlor 600 are almost identical (2).

Some of the most comprehensive information on PCB use comes from the United States, where most PCBs were produced for capacitors (~45% of sales) and transformers (~25% of sales), with ~20% of sales attributed to plastics

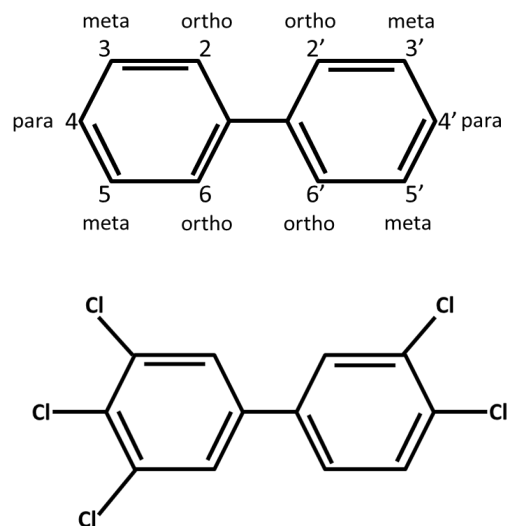


Figure 1: PCBs have the basic chemical formula $C_{12}H_{10-n}Cl_n$, where n is the number of chlorine atoms present in the molecule. (Top) The numbering of the biphenyl molecule shows where a chlorine atom may be attached. (Bottom) Chemical structure of PCB-126 (3,4,5-3',4',5'-CB).

and hydraulic lubricants, and minor uses; the remaining ~10% were exported (8). Limited data are available for PCB use in the UK. The UK Soil and Herbage Survey (6) identified that approximately 66,500 tonnes of PCBs were manufactured between 1954 and 1977, of which around 27,000 tonnes were exported to other countries. However, there were no figures for quantities imported to the UK. Of the 40,000 tonnes of PCBs sold in the UK since 1954, only about 400 tonnes are now present in the environment, with the remainder either still in use, transported away from the UK, or degraded/transformed (6). Thus even with the

cessation of production and use, risk assessment of PCBs remains an important issue in the UK.

Chemical analysis

Due to the structural similarity of PCBs, compound-specific analysis is a significant analytical challenge. Early methods for PCB analysis involved non-selective techniques such as gas chromatography electron capture detector (GC-ECD). These techniques normally involved the analysis of total PCBs in technical mixtures like Aroclors. However, pure technical mixtures are rarely present in the environment, because PCBs undergo post-depositional changes and are present along with other chemically similar contaminants. PCBs were first detected as interferences in organochlorine pesticide analysis in GC-ECD chromatograms, and it took almost seven years to identify and confirm PCBs as the environmental contaminants (9). Since the 1980s, advances in mass spectrometry have led to the development of congener specific methods. Bench-top quadrupole mass spectrometers became commercially available in the 1980s and are still present in most laboratories today. Quadrupole mass spectrometers are considered to be low-resolution instruments and are typically limited to unit mass resolution, which cannot distinguish between two similar compounds with a difference in atomic mass of less than 0.5 Da. The development of high resolution spectrometers such as time-of-flight mass spectrometers (TOF-MS) significantly improved the selectivity of PCB analysis.

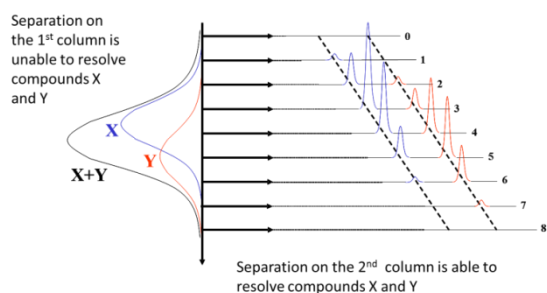


Figure 2: GCxGC analysis enables rapid sampling of the analytes eluting from the first column to be re-injected into the second column. The columns have different stationary phases allowing for an extra dimension of separation. Figure adapted from reference 9.

In contaminated-land investigations, PCB are commonly analysed using GC-MS, which provides a relatively quick screen and can show whether a sample has been grossly contaminated. Limits of detection vary with different commercial laboratories but are generally in the range of 10 to 1000 $\mu\text{g kg}^{-1}$; few labs can provide limits of detection below 1 $\mu\text{g kg}^{-1}$. This can be a significant limitation, because background total PCB concentrations in UK urban soils are between 0.01 and 40 $\mu\text{g kg}^{-1}$ (6).

Sample clean-up and high-resolution mass spectrometry techniques can now remove many interfering compounds, such as dioxins, furans and organochlorine pesticides, but they cannot stop some PCBs from co-eluting with other PCBs.

The EC7 congener mixture is a set of PCBs, commonly encountered in environmental samples, consisting of PCBs 28, 52, 101, 118, 153 and 180 (10, 11). The co-elution of the EC7 compounds highlights of the main limitations of PCB analysis using GC-MS: the inability of the chromatography to fully resolve the target compound. The development of comprehensive two-dimensional GC (GCxGC-TOFMS) techniques solved most of these problems. By combining two GC columns with different stationary phases, it adds an extra dimension to the analysis (Figure 2). Using GCxGC-TOFMS, analysts can separate the target PCBs (12) with detection limits in the attogram range (10^{-18} g) (13). These techniques allow detection and quantification of individual PCB concentrations in humans from just a single blood spot.

Human health risk assessment

The European Food Safety Agency (EFSA) (14) states that 130 of the 209 PCB congeners have been reported in various commercial preparations (such as Aroclors) and environmental samples. However, the UK preferred methodology for risk assessment is to look at the WHO12 (PCBs 77, 81, 126, 169, 105, 114, 118, 123, 156, 157, 167 and 189) congeners only. This subgroup comprises coplanar congeners that are believed to show a dioxin-like toxicity. The UK Environment Agency (15) does not consider the WHO12 to be carcinogens. It is believed that most of the toxic effects from dioxin-like PCBs result from their binding to the aryl hydrocarbon receptor, which can cause immune suppression, reproductive and developmental toxicity. Non-dioxin-like PCBs are also toxic and have been shown to elicit neurological, endocrine and immunological effects (14). The non-dioxin-like PCBs are ~5 times more abundant than the WHO12 in food (14) and ~4 times more abundant in soils (6). Therefore, many other worldwide organisations prefer to monitor both dioxin-like and non-dioxin-like PCBs.

The more common occurrence of EC7 over WHO12 congeners is primarily due to their greater percentage weight concentrations in commercial mixtures. The EC7 congeners make up ~20% by weight of PCBs in commercial Aroclor mixtures, whereas the WHO12 make up <4% by weight (Frame, 2001). Thus, even when taking into account degradation within environmental samples, the EC7 are more commonly found in higher concentrations in environmental and food samples.

The UK approach to human health risk assessment of PCBs is to screen and carry out detailed quantitative risk assessments using only the WHO12. However, due to their toxicity and higher environmental concentrations there is an argument for the non-dioxin-like PCBs to also be

considered. Commercial laboratory analysis of the EC7 is less expensive and more likely to detect PCBs in measurable concentrations than analysis of the WHO12. Therefore, screening of contaminated land using the EC7 and detailed risk assessment using both the EC7 and WHO12 is likely to provide a clearer picture of the risks posed by PCBs to humans and the environment.

When considering human exposure pathways, vegetation uptake of PCBs from soil by plants is generally negligible; PCB concentrations in plants more closely reflect atmospheric deposition (16). Most PCB uptake from contaminated land in the UK is considered to be *via* the soil medium by direct contact with skin and by direct and indirect soil ingestion, with insignificant inhalation of particulates or vapour. For risk assessment purposes in the UK, only combined oral and dermal exposure is considered, with the assumption that the dominant pathway is the oral route. Therefore, a Tolerable Daily Intake (TDI) is set for this exposure pathway only (15).

Because the dioxin-like PCBs have additive health effects, Toxic Equivalency Factors (TEFs) have been assigned to each congener, based on comparison with the most potent dioxin, 2,3,7,8-TCDD. The TEFs agreed by the World Health Organization (WHO) in 2005 are used by the Environment Agency for human health risk assessment (15). Compared to a TEF of 1 for the dioxin 2,3,7,8, TCDD, the TEFs for PCBs range from 0.1 to 0.00003. When producing a Soil Guideline Value (SGV) for PCBs, the Environment Agency followed many of the findings of Van den Berg *et al.* (17). The Environment Agency decided that the risks from dioxins/furans and dioxin-like PCBs should not be assessed against one TDI. Instead the congener mixture should be characterised and the fate and transport of each congener modelled. The TEFs for each congener are applied and assessed against an oral TDI for dioxin-like compounds

of 2 pg WHO-TEQ kg⁻¹ BW day⁻¹. To produce an SGV for screening purposes, the Environment Agency used the UK Soil and Herbage Survey data (6) to produce an estimate for the composition of the PCB mixture. Therefore, the UK apply an SGV of 0.008 mg kg⁻¹ to dioxins/furans and dioxin-like PCB presence for a residential setting (6% soil organic matter). However, using the same scenario based on the EC7 PCBs (using the toxicity of PCB 118 as a conservative estimate), a screening value of 0.73 mg kg⁻¹ was calculated. Regardless of which method is used to generate a screening value for the EC7, analysis of these compounds could aid decision making process when undertaking human health risk assessments.

Forensic techniques

PCBs are well known for their resistance to degradation. However, once they have entered soils and sediments they can undergo subtle transformations, because not all congeners are degraded at the same rate. This can alter the original PCB signature and complicate source identification. If the processes altering the signature are understood then it may be accounted for and in some instances used to help age the contamination event. Use of environmental forensics techniques in contaminated land investigations can help answer many of these questions that are sometimes overlooked.

Forensic investigations involving PCBs are not limited to soils and sediments and can often involve humans and other animals. This adds further complexity to the source identification process, because further subtle transformations to the PCB signature can occur in animals. Collecting wildlife specimens for PCB analysis presents ethical, scientific and practical challenges. There are alternatives to organ collection and dissection; many investigations into PCB signatures have been undertaken on eggs, feathers, hair and serum (16).

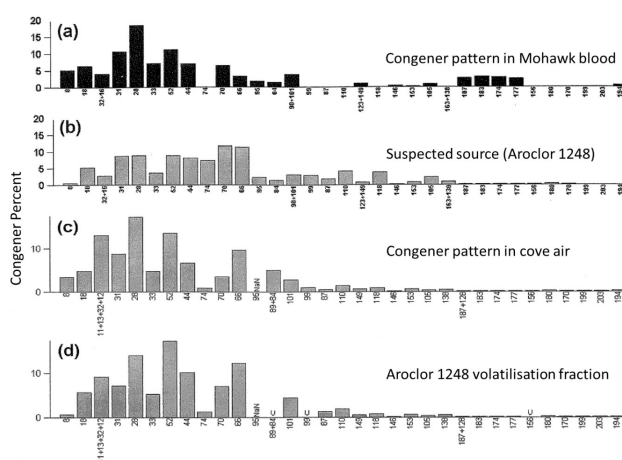


Figure 3: Adapted from Johnson *et al.*, (2006), (a) a subset of Akwesasne Mohawk blood samples (the receptor). (b) Unaltered Aroclor 1248, the suspected primary source of exposure that was used at aluminium foundries close to the site. (c) A composite ambient air sample obtained from a cove adjacent to Akwesasne. (d) The volatile fraction of Aroclor 1248 as observed in volatilisation experiments.

When assessing human exposure to PCBs, an individual with background exposure will have high proportions of PCBs that are more resistant to biotransformation and elimination. These include PCBs with a higher degree of chlorination and co-planar PCBs with no *ortho* chlorines. However, the exact position of chlorine atoms on the biphenyl is also important in determining the retention of PCBs in humans (18). This information can be used to account for changes in the PCB signature between source and receptor. The extent of these changes could also be used to help age date human exposure to PCBs. When undertaking environmental forensic investigations of PCBs in humans and other animals it is important to consider how

the results from soil samples, non-invasive sampling of humans and other animals can be undertaken. There is debate around the detrimental effects of obtaining samples from humans during contaminated land investigations. However, when such sampling is handled sensitively with clear communication, the benefits can outweigh the potential costs. Analytical results from the receptors themselves will provide additional and potentially better information on the risks posed by PCBs. The results can allow for a better estimation of risk to the individual along with the potential for source identification and age dating the exposure.

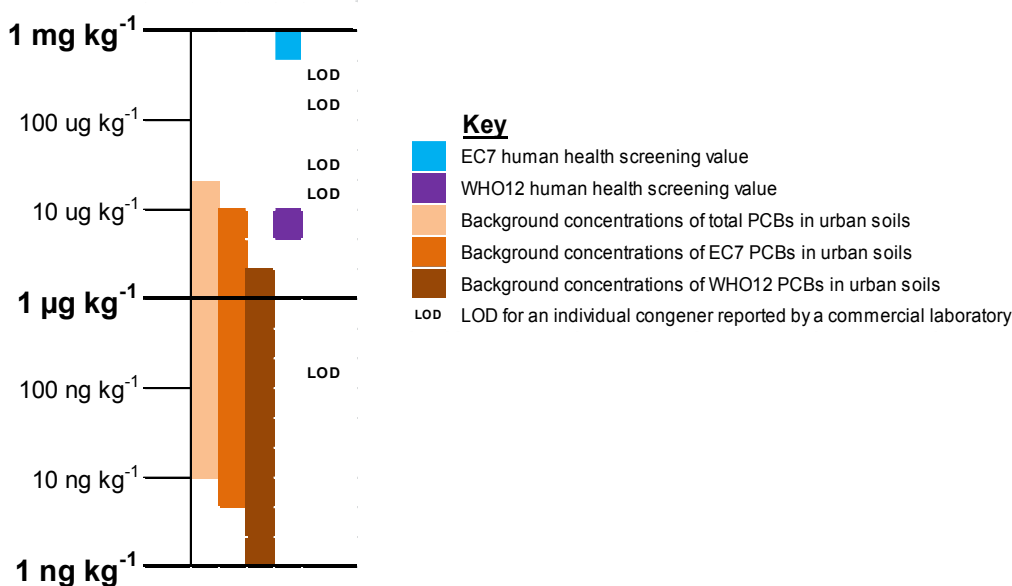


Figure 4: The range of likely background concentrations for PCBs in soils, relevant UK human health screening values for PCBs in soils and the limits of detection (LOD) reported by several commercial laboratories for the analysis of PCBs in soils.

the congener profile may be altered between the source and receptor. Along with post depositional changes in the environment, changes in exposure pathways (oral, inhalation or dermal intake) plus post uptake processes, such as biotransformation and elimination, can all alter the PCB signature. **Figure 3** shows the difference in the PCB signature between source, pathway and receptor from a case study on Mohawk Indians in the United States of America (2). The differences between the source material and Mohawk blood can be explained by processes such as volatilisation and metabolism. The results showed a reasonable match between the Mohawk blood and the ambient air and A1248 volatilisation patterns, which the authors used along with other data to indicate that inhalation A1248 vapours was a significant route of exposure.

The techniques used in forensic investigations of PCBs in humans and animals could be of great benefit to human health and environmental risk assessments. To supplement

Summary

The analysis and investigation of PCBs has advanced substantially in recent decades. From the detection of PCBs as contaminants on ECD traces in the 1970s, quantification of background concentrations of individual PCBs is now possible at the attogram level, allowing accurate quantification in sample volumes of less than 1 mL. Despite these advances, due to cost constraints the focus in contaminated land investigations is too often placed on fast analysis and screening of the WHO12 PCBs, with limits of detection that are not fit for purpose. **Figure 4** presents the limits of detection of several commercial laboratories showing that they are not adequate when assessing human health risks of the WHO12 PCBs from soils. An accurate human health risk assessment cannot be undertaken by comparing a PCB concentration of $<100 \mu\text{g kg}^{-1}$ to a screening value of $8 \mu\text{g kg}^{-1}$.

When analytical results are obtained with an appropriate limit of detection, results for the WHO12 and EC7 congeners are of great value in the initial phases of human health risks assessments. Background concentrations of PCBs are unlikely to pose a significant risk to human health, but when PCBs are found to pose a risk to human health, identifying the source of contamination assists assessors with choosing the most suitable remediation technique. The WHO12 congeners make up less than 4% of the total PCB content in commercial mixtures and are of little diagnostic value for source identification. Considering the presence of other PCBs and demanding lower analytical limits of detection, will produce more useful information, which can be used to make more informed decisions in contaminated land investigations.

References

1. M. D. Erickson, 'Introduction: PCB properties, uses, occurrences and regulatory history'. In L. W. Robertson and L. G. Hansen (Editors), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, University of Kentucky Press, 2001.
2. G. W. Johnson, J. F. Quensen III, J. R. Chiarenzelli and M. Coreen Hamilton, 'Polychlorinated biphenyls', in R. D. Morrison and B. L. Murphy (Editors), *Environmental Forensics: Contaminant Specific Guide*, Academic Press, 2006.
3. M. A. McKinney *et al.*, 'Flame retardants and legacy contaminants in polar bears from Alaska, Canada, East Greenland and Svalbard, 2005-2008', *Environment International*, 2011, **37**, 365-374.
4. C. D. Sandau *et al.*, 'Comprehensive solid-phase extraction method for persistent organic pollutants. Validation and application to the analysis of persistent chlorinated pesticides', *Analytical Chemistry*, 2003, **75**, 71-77.
5. J. U. Skaare *et al.*, 'Organochlorines in top predators at Svalbard: occurrence, levels and effects', *Toxicology Letters*, 2000, **112**, 103-109.
6. C. S. Creaser, M. D. Wood, R. Alcock, D. Copplestone and P. J. Crook, *UK Soil and Herbage Pollutant Survey Report No. 8. Environmental Concentrations of Polychlorinated Biphenyls (PCBs) in UK Soil and Herbage*, Environment Agency, 2007.
7. I. Holoubek, 'Polychlorinated biphenyl (PCB) contaminated sites worldwide'. In L. W. Robertson and L. G. Hansen, (Editors), *PCBs: Recent Advances in Environmental Toxicology and Health Effects*, University of Kentucky Press, 2001, pp 17-26.
8. R. L. Durfree *et al.*, 'PCBs in the United States – industrial use and environmental distribution', Agency UEP, 1976.
9. E. J. Reiner, K. L. Jobst, D. Megson, F. L. Dorman and J. F. Focant, 'Environmental forensics analytical methodology of POPs'. In G. O'Sullivan and C. D. Sandau (Editors), *Environmental Forensics for Persistent Organic Pollutants*, Elsevier, in press.
10. G. M. Frame, 'A collaborative study of 209 PCB congeners and 6 Aroclors on 20 different HRGC columns. 1. Retention and coelution database', *Fresenius Journal of Analytical Chemistry*, 1997, **357**, 701-713.
11. G. M. Frame, 'The current state-of-the-art of comprehensive, quantitative, congener-specific PCB analysis, and what we now know about the distributions of individual congeners in commercial Aroclor mixtures'. In L. W. Robertson and L. G. Hansen (Editors), *PCBs Recent Advances in Environmental Toxicology and Health Effects*, University Press of Kentucky, 2001, pp 3-9.
12. M. Harju, C. Danielsson and P. Haglund, 'Comprehensive two-dimensional gas chromatography of the 209 polychlorinated biphenyls', *Journal of Chromatography A*, 2003, **1019**, 111-126.
13. D. G. Patterson, S. M. Welch, W. E. Turner, A. Sjodin and J. F. Focant, 'Cryogenic zone compression for the measurement of dioxins in human serum by isotope dilution at the attogram level using modulated gas chromatography coupled to high resolution magnetic sector mass spectrometry', *Journal of Chromatography A*, 2011, **1218**, 3274-3281.
14. European Food Safety Authority, 'Results of the monitoring of non dioxin-like PCBs in food and feed', *EFSA Journal* 2010, **8**, 1701; <http://www.efsa.europa.eu/en/efsajournal/doc/1701.pdf>
15. Environment Agency, 'Soil Guideline Values for dioxins, furans and dioxin-like PCBs in soil', Science Report SC050021/Dioxins SGV, 2009; <http://www.environment-agency.gov.uk/static/documents/Research/SCHO0909BQYQ-e-e.pdf>
16. V. L. B. Jaspers, D. Megson and G. O'Sullivan, 'POPs in the terrestrial environment'. In G. O'Sullivan and C. D. Sandau (Editors), *Environmental Forensics for Persistent Organic Pollutants*, Elsevier, in press.
17. M. Van den Berg *et al.*, 'The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds', *Toxicological Sciences*, 2006, **93**, 223-241.
18. D. Megson *et al.*, 'Elucidating the structural properties that influence the persistence of PCBs in humans using the National Health and Nutrition Examination Survey (NHANES) dataset', *Science of the Total Environment*, 2013, **461-462**, 99-107.

Acknowledgements

The authors thank Sean Comber (Plymouth University) and Kate Canning (Arup) for constructive comments whilst reviewing this article.

DAVID MEGSON and SARAH DACK

School of Geography, Earth and Environmental Science, Plymouth University, Devon PL4 8AA
E-mail: david.megson@plymouth.ac.uk

Can mineral carbonation be used for industrial CO₂ sequestration?

The imperative to sequester CO₂ emissions from fossil fuel burning on a large scale is well recognized. Mineral carbonation is already deployed commercially and is economically viable for niche industrial outlets, but the process is not suitable, at present, for large scale applications such as power stations.

Introduction

Mineral carbonation is already deployed commercially and is economically viable for some niche industrial operations. But the technology is not yet suitable for effectively removing CO₂ in large scale processes such as power stations. This was the conclusion of an ESED-sponsored workshop on CO₂ mineralisation held on 28 November 2012 at Burlington House, London (1). However, mineral carbonation could become a significant contributor to carbon capture and storage (CCS) if:

- the technology can be further developed to reduce net process energy use;
- saleable carbonated products suited for low-value mega-tonne scale markets can be manufactured;
- and flue-gases can be mineralised directly.

At the moment, mineral carbonation R&D is on the edge of CCS policy, but without investment in more and focussed R&D, it cannot achieve its promise.

CO₂ mineralisation is one of the cross-disciplinary cluster targets identified by the EPSRC-funded CO₂Chem Network (co2chem.co.uk). The First International Conference on Accelerated Carbonation for Environmental and Materials Engineering, initiated by the UK company Carbon8 Systems Ltd, was held at the Royal Society in London in 2006; the most recent (ACEME13) was held in April 2013 in Leuven, Belgium. CO₂Chem Network formed its mineralisation cluster in April 2012. The above mentioned meeting at Burlington House was this cluster's first workshop (1). The workshop brought together about fifty active academic and industrial researchers from more than forty organisations from around the UK, plus five overseas delegates.

What is mineral carbonation?

Mineral carbonation is an approach to permanent CO₂ sequestration that involves reactions of magnesium or calcium oxides (from mineral silicates or industrial wastes, rather than limestone) with CO₂ to give inert carbonates. Due to the lower energy state of carbonates compared to CO₂, these reactions release significant amounts of energy and, in nature, occur spontaneously (but slowly). Vast

amounts of suitable and readily accessible mineral silicates exist – many times more than is needed to sequester all anthropogenic CO₂ emissions.

The slow speed of reactions of natural silicate rocks (requiring mechanical, chemical or biological activation) and the large amounts of minerals or wastes that must be handled (2-3 tonnes of rock per tonne of CO₂) are the main challenges for commercially viable industrial mineral carbonation applications. Processes that accelerate kinetics and maximise materials values with minimal additional costs and environmental impacts are the focus of academic research and commercial development around the world.

Mineral carbonation offers a commercial route to scalable CCS, starting with bottom-up, market-driven and highly profitable distributed niche applications where cost-reduction learning curves apply. Valuable and useful by-products such as silica, metals, chemicals, cements and construction materials, as well as remediation of negatively valued waste feedstocks, enable a business case to be made for CO₂ sequestration even where there is no carbon price (**Figure 1**).

Mineral carbonation processes are increasingly being developed to sequester CO₂ directly from flue gases rather than from pure CO₂. This bypasses the energy-intensive and costly solvent capture/regeneration step of conventional geo-CCS and avoids the infrastructure and public acceptability challenges of supercritical CO₂ pipeline transport and geological storage.

What needs to be done?

To develop mineral carbonation into a deployable engineering solution for large-scale CO₂ sequestration, R&D should be focussed in three main areas.

Energy life-cycle analysis. In principle, the reaction of Mg/Ca silicate minerals with CO₂ to form carbonates and silica is exothermic and spontaneous, releasing ~0.5MWh per tonne CO₂ sequestered. In practice, though, the reactions of the natural minerals are very slow (and vary significantly between them), and energy-intensive treatments, chemical additions or process conditions are applied to accelerate carbonation and recover process reactants. There are many ways to accelerate the kinetics, leading to a

myriad of different mineral carbonation processes being proposed (2). Very few of these processes have been analysed to understand how much CO₂ they generate for every tonne of CO₂ that they sequester. The key challenge is to

within conventional CCS. It makes little economic or technical sense to capture CO₂ first and then to mineralise it. The third area for R&D focus thus is the mineral sequestration of CO₂ directly from flue gas. Yet, most research publications,

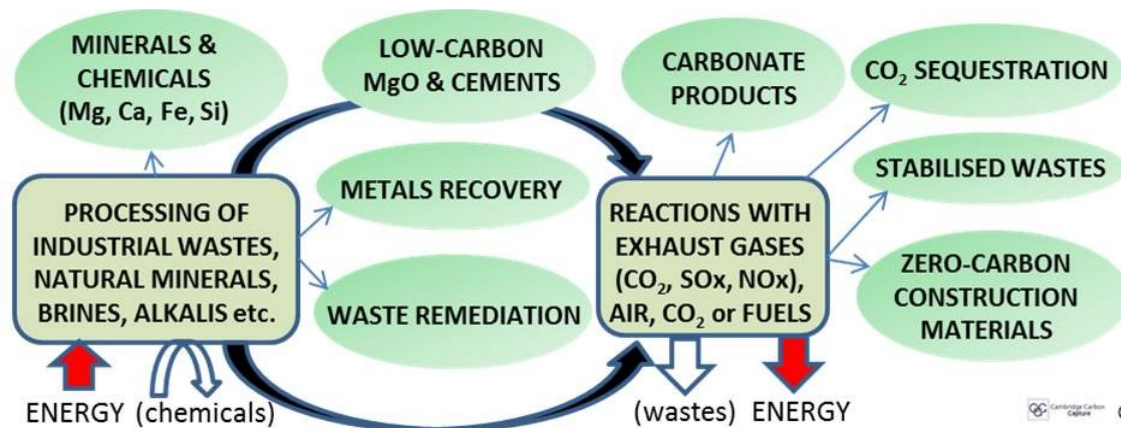


Figure 1: Pathways to mineral carbonation. Multiple business opportunities in products and services drive different choices of process and materials flows, with CO₂ sequestration as one of several outputs.

develop better mineral carbonation chemistries and process engineering schemes that minimise the net life-cycle energy required to sequester a tonne of CO₂ as carbonate. This will include investigation of catalysts, recovery of energy released in carbonation, and recovery and recycling of process additives.

Scalability. At least two tonnes (and in some processes up to ten tonnes) of product materials are generated for every tonne of CO₂ sequestered through carbon mineralisation. In today's niche commercial deployments, these products—such as silica, magnesium carbonate or stabilised aggregate—are generally valuable and can be sold into available markets.

At much larger scales, for example a 0.5 GWe coal-fired power station producing ~3 million tonnes CO₂ per year and 6 to 10 million tonnes per year of mineral carbonation products, more mineral feedstock than coal needs to be mined and transported to the site, and it becomes much more difficult to find sufficiently large markets into which to sell the carbonation products. In China, a 1.2 GWe coal power station is planned to be fitted with mineral carbonation technology supplied by Peabody and Calera. In this case, the carbonation products will be formatted as low-carbon construction blocks to build an adjacent new city. If mineral carbonation processes are going to be successfully applied to large scale CO₂ sequestration, R&D is needed to match product materials characteristics to the technical requirements of locally available markets.

Dilute CO₂. Post combustion capture of pure (>90%) CO₂ from flue gas using regenerable solvents/sorbents is recognised at the single most costly and energy-intensive step

funding calls and policy-level discussions in mineral carbonation are based on the premise of capture followed by mineralisation.

Mineral carbonation needs to be considered very differently from conventional geological CCS. Unlike CCS, carbonation is fundamentally an exothermic process, which is a much better starting place. It is profitable and commercially deployed at small scale, which CCS is never expected to be able to achieve. As a market-driven modular technology, it resembles wind turbines or solar power, which reduce in cost by 22% for each doubling of capacity and were once considered as unfeasibly expensive niche technologies. Like these technologies, carbon mineralisation has the potential to benefit strongly from learning curves. Given the right R&D support and market incentives, mineral carbonation has the potential to become a viable alternative to geological CCS and more than a feasible option for industrial CCS.

References

1. See <http://www.rsc.org/Conferencesandevents/conference/>; for speaker presentations contact network@co2chem.co.
2. M. D. Torrontégui, 'Assessing the Mineral Carbonation Science and Technology', Master's Thesis, Institute of Process Engineering, ETH Zurich, Zurich, Switzerland; available online.

MICHAEL PRIESTNALL

Cambridge Carbon Capture Ltd.,
Hauser Forum,
Charles Babbage Road,
Cambridge CB3 0GT
Michael.priestnall@cacaca.co.uk

Forthcoming Symposium

RSC Environmental Chemistry Group & RSC Environment, Sustainability & Energy Division

2014 Distinguished Guest Lecture & Symposium

Plastic debris in the ocean – a global environmental problem

A one-day symposium organised by the Environmental Chemistry Group and Environment, Sustainability and Energy Division of the Royal Society of Chemistry. The **2014 ECG Distinguished Guest Lecture** will be given by **Professor Richard Thompson** (Plymouth University).

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

When: **Wednesday 12th March 2014**

Programme

1200 Lunch, Coffee

1300 Meeting to be opened by Dr William Bloss (Chair of ECG)

Professor Norman Billingham (University of Sussex)

Polymers and their environmental degradation

Dr Edwin Foekema, IMARES (Institute for Marine Resources and Ecosystem Studies)

Aspects that determine the actual risk of plastic associated POPs for marine organisms

1430 Tea/coffee; **ECG Annual General Meeting**

1530 **Dr Heather Leslie, Institute for Environmental Studies, VU University**

Macroplastics and microplastics – what is their environment impact?

2014 ECG DGL: Professor Richard Thompson, Plymouth University

Plastic debris in the ocean – solutions to a global environmental problem

General Discussion

1715 Close

To register online, or download a hard copy registration form, please see www.rsc.org/ecg and choose "Forthcoming Events". For further details please contact s.t.wagland@cranfield.ac.uk

Registration fees

- Non-members of ECG – £90 (£50 early bird rate- all bookings before 31st January)
- ECG members and concessions – £45 (£30 early bird rate- all bookings before 31st January)
- Retired RSC and ECG members – Free (limited availability)

A limited number of places are reserved free for retired members; these will also be allocated on a first come, first served basis. We are able to offer a limited number of travel bursaries for current students – please contact the symposium organiser if you would like to be considered for one of these.

Meeting Report

Tropospheric aerosol: formation, transformation, fate and impacts

A report on *Faraday Discussions* 165 held at Leeds University from 22 to 24 July 2013.

Atmospheric aerosols are a ubiquitous phenomenon, but achieving an understanding of both their formation and their subsequent changes in morphology and composition is a bewitching challenge. They are formed from both anthropogenic and biogenic sources, but under appropriate conditions, either of these can achieve local and temporal dominance; and they have long been associated with significant (but uncertain) contributions to climate change. They are implicated in the long-range transport of organic and inorganic chemicals, and because of their size, composition and distribution, they are profoundly important for human health. This conference, attended by about ninety delegates from Europe, the US, Bahrain, Brazil, China and Japan, described and discussed recent advances and developments in probing, analysing and assessing their physicochemical behaviour.

Spyros Pandis (Carnegie Mellon) gave the opening address, “*Atmospheric aerosols – insights from the combination of field measurements and regional chemical transport models.*” He drew attention to the complexity of the systems under investigation, with variations of twelve orders of magnitude in mass, great spatial and temporal variability (the former notable for the aerosol singularities belonging to cities and the latter ultimately driven by the sun), and thousands of chemical reactions. He pointed out that increases in aerosol mass were driven by different processes from those which increase aerosol size, and that an understanding of these differences is a fundamental issue for the field. Other outstanding issues are linked to atmospheric nitrate (e.g. its variation with altitude and understanding the role of the oceans in nitrate resuspension) and organic aerosols (their chemical nature, volatilities, and O:C ratios; the level of oxygenation acts as a probe for the reaction history of the aerosol organic component). He went on to discuss how field campaigns, including Zeppelin flights over Germany/Italy (2012) and Scandinavia/Finland (2013), collect data that aid the evaluation of models/simulations and showed how the results drew attention to aerosol ageing, aerosol transport times, and changes in aerosol number as targets for elucidation.

Several talks examined the growth of aerosols. For example, **Tinja Olenius et al.**'s talk was on “*Comparing simulated and experimental molecular cluster distributions.*” This work looked at clusters formed by small numbers of molecules and found good agreement between the modelled steady state concentrations of negative cluster ions and experimental results obtained at CERN. **Mijung Song et al.**

reported on “*Morphologies of mixed organic/inorganic/aqueous aerosol*” and concluded that: “Based on the present evidence, a ‘core-shell’ morphology is the prevalent configuration of liquid-liquid phase-separated tropospheric organic/ammonium sulfate/H₂O particles.” **Nadine Hoffmann et al.** spoke on “*Contact freezing efficiency of mineral dust aerosols studied in an electrodynamic balance: quantitative size and temperature dependence for illite particles*”, reporting “the first quantitative measurements of the freezing probability of a supercooled droplet upon a single contact with a size selected illite mineral particle.” Further talks on this topic included **Daniel Knopf** and **Peter Alpert** reporting on “*A water activity based model of heterogeneous ice nucleation kinetics for freezing of water and aqueous solution droplets*,” and **Neil Donahue et al.** presenting a quantum mechanical study of cluster stability in a talk entitled “*How do organic vapours contribute to new particle formation?*”

Other researchers explored the chemistry that occurs on or in an aerosol during its life. In their talk on “*Organic aerosol formation photo-enhanced by the formation of secondary photosensitizers in aerosols*,” **Kifle Aregahegn et al.**, concluded that “In the atmosphere, glyoxal and potentially other gas precursors would thus produce efficient photosensitizers in aerosol and autophotocatalyze SOA growth” (SOA = secondary organic aerosol). **Jacqueline Hamilton et al.** spoke on “*Online and offline mass spectrometric study of the impact of oxidation and ageing on glyoxal chemistry and uptake onto ammonium sulfate aerosols*.” In their talk on “*Sulfate radical-initiated formation of isoprene-derived organosulfates in atmospheric aerosols*,” **J. Schindelka et al.** argued that their study “shows that sulfate radical-induced oxidation in the aqueous particle phase provides a reasonable explanation for the formation of these organosulfates from methacrolein and methyl vinyl ketone.”

Consequences of these changes on light absorption in the atmosphere were also reported by **Tan B. Nguyen et al.** (“*Brown carbon formation from ketoaldehydes of biogenic monoterpenes*”).

Field workers described their innovative and painstaking attempts to unravel the complexities of aerosol behaviour in a range of environments that differ in geography, demography and ecology. For example, **Bryan R. Bzdek et al.** spoke on “*Quantitative and time-resolved nanoparticle composition measurements during new particle formation*,” **Paulo Artaxo et al.** on “*Atmospheric aerosols in Amazonia and land use change: from natural biogenic to biomass*

burning conditions,” **M. Z. Jacobson** *et al.* on “*The effects of aircraft on climate and pollution. Part II: 20-year impacts of exhaust from all commercial aircraft worldwide treated individually at the subgrid scale,*” and Kelly Daumit *et al.* on “*Average chemical properties and potential formation pathways of highly oxidised organic aerosol.*”

Studies of the mechanisms of change occurring during the growth or ageing of aerosols were reported and gave insights into the chemical kinetics. In their talk on “*Tropospheric aerosol as reactive intermediate,*” **Agustín J Colussi** *et al.* concluded that “SOA is a key reactive intermediate.” **Carl Percival** *et al.* investigated “*Regional and global impacts of Criegee intermediates on atmospheric sulphuric acid concentrations and first steps of aerosol formation.*” **Wu Wang** *et al.* looked at “*Formation of secondary organic aerosol marker compounds from the photooxidation of isoprene and isoprene-derived alkene diols under low-NO_x conditions.*” In their study on “*Modelling the influence of alkane molecular structure on secondary organic aerosol formation,*” **Bernard Aumont** *et al.* used the GECKO-A (Generator for Explicit Chemistry and Kinetics of Organics in the Atmosphere).

Accurate measurement of aerosol properties (such as viscosity, diffusivity and surface tension) is essential for an understanding of the chemistry and assists the kinetic modelling of reaction schemes, although high viscosities and ill-defined reactions make such modelling demanding. Work has been done which addresses the need for these measurements via laboratory studies, including **Shouming Zhou** *et al.* (“*Kinetic limitations in gas-particle reactions from slow diffusion in secondary organic aerosols*”), **David Topping** *et al.* (“*Including phase separation in a unified model to calculate partitioning of vapours to mixed inorganic-organic particles*”), and **Naveen Hosny** *et al.* (“*Fluorescent lifetime imaging of atmospheric aerosols: a direct probe of aerosol viscosity,*” using fluorescence lifetime determination of viscosity-sensitive fluorophores termed molecular rotors).

Simulations can also help to understand aerosol properties, as shown for example by **Joseph Woo** *et al.* in a simulation using GAMMA (Gas-Aerosol Model for Mechanism Analysis), as reported in their talk entitled “*Aqueous aerosol SOA formation: impact on aerosol physical properties.*” **Kenneth Carslaw** *et al.* (“*The magnitude and sources of uncertainty in global aerosol*”) used the GLOMAP (GLOBAL Model of Aerosol Processes) model to suggest areas where measurements were of the greatest uncertainty and suggested these might be possible targets for future research.

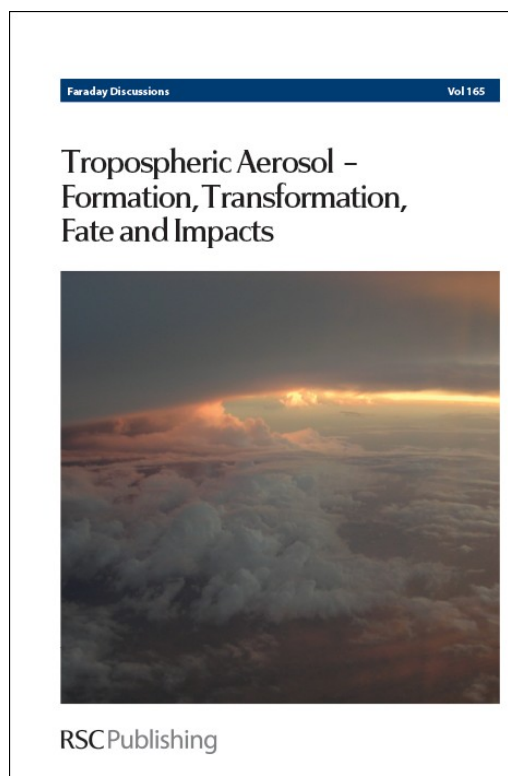
The published record of this meeting contains the papers described above and the extensive discussions about them. The papers contain the results from field measurements,

laboratory experiments and the outcomes from simulations and kinetic modelling, and there are detailed descriptions of the techniques used for aerosol chemistry initiation, product identification and quantification. But the discussions about the papers were incisive and in my view they undoubtedly moved the whole area forward. I recommend them to you.

LEO SALTER



Air Pollution and Traffic on Bridge Number 1, the first bridge over the Yangzi River in Wuhan, Hubei Province, China. Credit: Barnaby Chambers/Shutterstock.



Faraday Discussions, 2013, **165**, 1-572.

Meeting report

The science behind our cultural heritage

Report from an event held at the Institute of Physics, 76 Portland Place, London on 23 October 2013.

When we visit a historic house or art gallery we often take for granted the objects on display, without thinking about how they are preserved or how they change throughout the centuries. These twin talks provided a fascinating evening of interdisciplinary science in trying to understand these issues. A joint event of the IOP's Environmental Physics Group, the Royal Society of Chemistry's Environmental Chemistry Group and the IOP London and South East/REMS branches, this successful evening was attended by 50 people. The event was organised by EPG member **Brian Davies**.

Dr Nigel Blades (National Trust) started off the evening describing the challenge the National Trust faces. With over 1 million objects to display and 150 museums, it can be difficult to control the temperature and humidity of their surrounding environment while making houses accessible to visitors. Nigel explained the importance of relative humidity, that is, the relationship between the moisture content of the air and the content of the material they are trying to protect. Get it wrong, and you could end up with a mouldy painting, cracked lacquer, or warped wood. Get it right, and visitors will not even notice. A relative humidity between 40% and 65% is ideal for keeping artefacts in tip-top condition.

Nigel explained how sensors around a property record temperature and relative humidity, which vary over the course of the year. Staff can adjust the temperature to change relative humidity and thereby help to preserve artefacts. For example, Knole is a large property in Sevenoaks, Kent with fourteen purpose-built panelled rooms designed to display paintings and furniture. Built in an era of no central heating, Knole is well-ventilated and accustomed to cool temperatures. In a cool gallery environment, some environmental problems can be kept at bay, but when moved to a warmer, more humid environment, issues can emerge. For example, in one wooden artefact, larvae had remained dormant for many years, but then suddenly hatched when temperatures rose, leaving the artefact infested with small beetles.

It is not just the artefacts in houses that require preserving, but the buildings themselves. In Dunham Massey, Cheshire, Victorian-designed radiators kept parts of the house warm. The Victorians believed in fresh air, and therefore installed a vent to the outside at the bottom of one radiator mounted to an outside wall. Cold air coming through the vent was warmed by the radiator, providing heat to the room. However, if it was very cold outside, the incoming air could be rather chilly, and this became a problem at Dunham Massey.

Unknown to staff, a radiator of this type existed, and in a very cold winter a few years ago, where temperatures reached $-19\text{ }^{\circ}\text{C}$, the incoming air was so cold that the water inside the radiator froze, causing it to burst. Buildings such as this keep National Trust staff busy as they try to preserve them and the cultural heritage they contain within a changing environment.

Joe Padfield (National Gallery) works in a much more controlled environment, but he is a man with a problem. How do you display paintings in an efficient, well-lit environment so they can be seen, when light can potentially damage the paintings, for example causing colours to fade? Unlike the National Trust, the National Gallery only has to consider a few thousand masterpieces, yet these paintings are irreplaceable and of international importance.

In early 2013, newspaper reported that the sunflowers in van Gogh's famous painting were browner than first painted due to damage from LED lighting. Was this claim true? Joe explained how by taking tiny samples, a few tens of micrometers across, and viewing them under a microscope, conservationists can see how paint changes and fades. In the case of van Gogh's 'chrome yellow' sunflowers, the coating had indeed become browner with time. But were LED lights to blame? Throughout the lecture, the audience learnt about the different parts of the visible spectrum, and how lighting from parts of the spectrum can cause damage. LEDs were not convicted of wrong-doing; rather, it was ambient light throughout the years that caused the sunflowers to fade. You can find out more about spectral power distribution of light and Joe's research at <http://research.ng-london.org.uk/scientific/spd/>.

Joe explained that many pigments used in paintings can be affected by light. For example, in one several hundred-year-old painting, there was a lady looking into a dull grey sky. Yet chemical analysis of samples showed that the sky started off bright blue. Thus, if light can change the colour of a painting, it may portray a different meaning. Next time you visit a gallery or historical property, take a careful look at the ambient environment to see how it could influence the artefacts you see—there may be more science going on than you think.

Dr SALLY BROWN

IOP Environmental Physics Group/Department of Engineering and the Environment, University of Southampton

Meeting report

Environmental monitoring in the energy sector: exploring parallels between shale gas and nuclear

This event was held at the RSC's Chemistry Centre, Burlington House on September 26th 2013 under the auspices of the Environment, Sustainability and Energy Division. The meeting overviewed the current energy landscape with particular reference to shale gas extraction by fracking and then gave a perspective on the environmental challenges for shale gas extraction compared to those of the nuclear industry. The meeting, attended by fifty delegates, began with a welcome from **Dr Mindy Dulai** (Programme Manager Environmental Sciences, RSC). There were four speakers: **Professor Richard Clegg** (Chair) (MD Lloyd's Register Foundation), **Professor Richard Davies** (Dean of Knowledge Exchange and Impact and Director of Durham Energy Institute, Durham University), **Professor Fred Worrall** (Professor of Environmental Chemistry, Department of Earth Sciences, Durham University) and **Dr Matthew Randall** (Business Leader, Environmental Services Team, National Nuclear Laboratory).

In his introductory talk, **Professor Richard Clegg** pointed out that shale gas extraction by fracking creates land-based environmental issues with similarities to those generated by the nuclear industry, and that this suggests there are opportunities for knowledge transfer in areas such as geological/hydrogeological fracture flow modelling, the monitoring of gas evolution, post-closure risk assessment, clean-up and remediation, public engagement and stakeholder management. He welcomed the opportunity provided by the meeting to explore possibilities for the sharing of expertise and experience between the two industries.

Environmental risks associated with fracking were discussed in detail by **Richard Davies**, who spoke on "*Fracked or fiction: so what are the risks?*" He focused on the way in which several aspects of risk in the shale gas extraction industry can be assessed using existing evidence. He argued that this approach not only enabled public concern to be addressed effectively but also provided a sound basis for effective legislation. When compared to commonly exploited (or conventional) traps of oil and gas such as those in sandstone and limestone, shale is often referred to as an unconventional source, because the technological challenge of working with the low permeability of the fine-grained source rock has made extraction commercially unattractive

in the past. The nature of the reservoir is considered therefore unconventional. However, since the 1990s, hydraulic fracturing ("fracking") of the Barnett Shale in Texas has been performed on a large scale, using horizontal shafts drilled off from the main vertical shaft to introduce water under pressure to create fractures from the horizontal sections. This approach has a primary environmental problem: not only are large volumes of water used but, depending on the particular well and the operating processes being applied, 10% to 50% of the water comes back to the surface as "flow-back." This water can be contaminated with dissolved material/brine that shows measurable but low (1% above background) levels of radioactivity associated with uranium, radon, radium and thorium (arsenic concentrations are also elevated). Sourcing and treating the volumes of water involved is not without issues for local water suppliers and their treatment plants.

As well as the environmental problems associated with the sourcing and disposal of water, fracking has created public concern in relation to earthquakes and the contamination of water supplies. Richard Davies used the evidence available from hundreds of thousands of well-head operations to show that fracking-induced seismic events were not only rare (a total of three have been recorded so far; Canada, USA and Blackpool) but also small (1.5 to 3.5 on the Richter Scale), below those from conventional oil and gas extraction (events up to magnitude 5) or dam filling (magnitude 7 to 8). He also showed that the contamination of water supplies by leakage through well walls was of low probability. In the Barnett Shale area, for instance, thousands of feet separate the fractures from the sub-surface water supplies above them. In general, fractures have only a 1% chance of being greater than 300 m, and aquifers lying above much deeper horizontal well shafts are therefore unlikely to be contaminated by well water.

However, without the appropriate legislation and controls, well integrity (sealing after use) could become a much more serious issue. Typically, a small well-head will operate for up to a decade before being abandoned. As in the nuclear industry, a form of decommissioning is required to protect the environment for generations. Cement seals can corrode and crack, as can the steel components of the well that re-

main *in situ* after abandonment. There will be a large increase in the number of shale gas wells drilled in the UK (from 1902 to 2103, the UK drilled nineteen wells a year, but shale gas extraction could result in up to 500 wells drilled per year). Studies of abandoned wells suggest that leaks are probable, and given the number of wells likely to be in operation in the UK in the future, knowing their precise location and monitoring them post-operation is vital if their integrity is to be assured.

Fred Worrall spoke next (“*Environmental impacts of shale gas – things we do not know*”). He suggested that shale gas extraction should be categorised as industrial development in a rural area – an approach that draws out the ways in which fracking in a relatively small and congested country like the UK has a different impact compared with wells in the USA. Impacts on habitats, air quality (e.g. methane), water resources (quality and quantity; each new well has a water and waste demand equivalent to an extra population of 350 people), well integrity, public safety, agriculture and quality of life are all aspects of fracking about which little or nothing is known in the UK context. For instance, each well pad has a direct footprint of 9 acres and an indirect footprint of 21 acres and it is not known how much land is needed to minimise the impact of spills and leaks, whether riparian buffer zones should be mandatory, what the environmental consequences of increased construction and transport might be, and whether effects on animals would be significant—in the USA, ‘zero discharge’ requirements mean that well pads are being bundled to achieve the last mentioned. Apart from the impacts of transport to and from the well, air quality is mostly impacted by methane emissions and it needs to be established how these emissions compare to those produced from coal mines, landfill and conventional onshore oil and gas extraction before a useful estimate of the operational air quality risk can be made for shale gas extraction.

The final presentation was from Matthew Randall (NNL), who talked on “*Environmental monitoring in the nuclear industry: underpinning clean up and remediation*”, chiefly using Sellafield as a case study. The approach to environmental monitoring and assessment on the site (e.g. leakage and legacy storage issues) involves the integration of modelling with monitoring, environmental assessment and experimental data. Hence, boreholes at different depths in and around the source with γ -loggers, ERT monitoring (Electrical Resistance Tomography measurements of ionic strength/salinity), and gas monitoring are used around the low-level-waste repository to inform the modelling of plumes of low-flow contamination from the source. Ion chemistry was investigated by analysis and areas of large charge imbalance were indicative of challenges to the integrity of the monitoring. The data were used in a GIS (Geographic Information System) environment to produce a 3D visualisation of groundwater contaminant plumes which was integrated with 3D geological modelling of the superficial and bedrock geology underlying the Sellafield site.

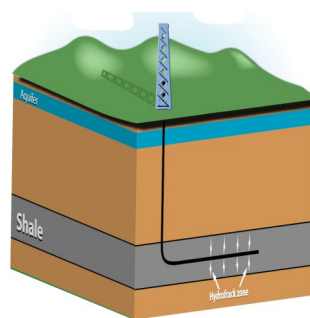
Given that leakage from abandoned shale-gas wells will almost certainly produce legacy problems associated with excursions of waste water and other material into the surrounding geological environment, this approach to long-term monitoring and assessment by the nuclear industry has a real relevance and applicability to shale gas extraction.

Matthew pointed out that the different chemical species in plumes needed to be assessed in terms of their persistence – radioactive lifetimes, mobility, reactivity in different geological environments etc. (MNA – Monitored Natural Attenuation). At Sellafield, some species (e.g. actinides) stay close to the source but others (such as ^{14}C , ^{99}Tc , and ^{90}Sr) are predicted to have a greater impact on groundwater. Speciation (e.g. ^{99}Tc is mostly present mostly as TcO_4^-) is also important for the mobility of contaminants through the geology (e.g. illite clay particles have significant numbers of high affinity edge sites and therefore a high capacity for immobilising ions). In fracking, the release of oxidising fluids into a reducing environment will cause complex speciation issues in the flowback water; for instance, arsenic remobilisation can occur as a consequence of the redox chemistry.

The meeting led to a good and informed discussion, the openness and lack of confrontation in the exchanges being particularly notable. A particular point of relevance was the comment that Bowland Shale in the UK was considerably thicker than that at US sites and that because of the way that this changed the structural integrity of horizontal shafts, it held out the prospect that fewer well pads may be needed in the UK than in the USA (i.e. it was suggested that many more horizontal shafts could be run off a central vertical shaft in the UK than in the USA). It was also pointed out that in isolated rural areas, the subtle changes in point source emissions to air from abandoned well-heads (e.g. long term release of low concentrations of volatile organic compounds such as polycyclic aromatic hydrocarbons and other aromatic compounds) will need careful long-term monitoring during the lifetime of the well but most particularly after closure.

LEO SALTER

September 30th 2013



Credit: Laurie Barr/Shutterstock

Minamata Convention on Mercury

The Minamata Convention on Mercury, a global and legally-binding agreement to control and reduce emissions of mercury into the environment, was formally adopted by 141 nations at a Diplomatic Conference in the city of Kumamoto, Japan, in October 2013. The convention is expected to come into force within 3-5 years, and by the end of 2013 ninety-four nations, including the USA, had signed the agreement implying that they will abide by treaty regulations until it enters into force.

Minamata is a city within the Kumamoto Prefecture of Japan and is associated with Minamata disease, a neurological disorder identified in the 1950s in patients who had eaten seafood harvested in Minamata Bay and the Shiranui Sea (Yatsushiro Sea). Mercury (Hg^{2+}) discharges into the marine environment from a local chemical factory were identified as the cause of Minamata disease. The recognition that inorganic mercury is transformed into organomercury and bioaccumulates in the marine ecosystem led to an increased awareness from the 1990s onwards for the need to control mercury emissions into the environment.

Under the provisions of the Minamata Convention, Governments have agreed on a range of mercury-containing products whose production, import and export will be banned by 2020. These items have non-mercury alternatives that will be further phased in as these are phased out. They include:

- Batteries, except for ‘button cell’ batteries used in implantable medical devices;
- Switches and relays;
- Some compact fluorescent lamps;
- Mercury in cold cathode fluorescent lamps and external electrode fluorescent lamps;
- Soaps and cosmetics (mercury is used in skin-whitening products);
- Some mercury-containing medical items such as thermometers and blood pressure devices.

There will also be a ‘phase-down’ of dental fillings which use mercury amalgam.

Mercury from small-scale gold-mining and from coal-fired power stations represents the biggest source of mercury pollution worldwide. Under the Minamata Convention, Governments have agreed that countries will draw up strategies to reduce the amount of mercury used by small-scale miners and that national plans will be drawn up within three years of the treaty entering into force to reduce, and if possible eliminate, mercury. The Convention will also control mercury emission and releases from large-scale industrial

plants such as coal-fired power stations, industrial boilers, waste incinerators and cement clinkers facilities.

The US recently finalised a Mercury and Air Toxics Standard which is predicted to reduce mercury emissions by 20 tonnes by 2016, and an export ban came into effect in January 2013. The EU banned mercury exports in 2011.

Web links

- *Google* “Global Mercury Assessment 2013 - UNEP”
- Full text of the Minamata Convention: <http://www.mercuryconvention.org/Convention/tabid/3426/Default.aspx>

Further reading

- N. E. Selin, ‘Global change and mercury cycling: challenges for implementing a global mercury treaty’, *Environmental Toxicology and Chemistry*, Accepted Article; DOI: 10.1002/etc.2374.
- M. Chmiel *et al.*, ‘Organomercury compounds in environmental samples: emission sources, toxicity, environmental fate and determination’, *Critical Reviews in Environmental Science and Technology*, Accepted Article; DOI: 10.1080/10643389.2012.728825.
- H. Hsu-Kim *et al.*, ‘Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: a critical review’, *Environmental Science & Technology*, 2013, **47**, 2441-2456; [dx.doi.org/10.1021/es304370g](https://doi.org/10.1021/es304370g).
- C. T. Driscoll *et al.*, ‘Mercury as a global pollutant: sources, pathways, and effects’, *Environmental Science & Technology*, 2013, **47**, 4967-4983; DOI: 10.1021/es305071v.

RUPERT PURCHASE



Gold mining. Prospectors searching for gold on the Tonlé Sap river, Cambodia. Gold mining is one of the main sources of mercury in the environment. *Credit: Meunier/Shutterstock.*

ECG Environmental Briefs

Atmospheric chemistry at night

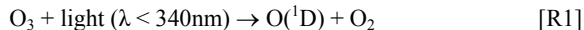
(ECGEB No 3)

Atmospheric chemistry is driven, in large part, by sunlight. Air pollution, for example, and especially the formation of ground-level ozone, is a day-time phenomenon. So what happens between the hours of sunset and sunrise?

This Brief examines the night-time chemistry of the troposphere (the lower-most atmospheric layer from the surface up to ≈ 12 km). Atmospheric chemistry is predominantly oxidation chemistry, and the vast majority of gases from emission sources are oxidised within the troposphere. The unique aspects of atmospheric oxidation chemistry at night are best appreciated by first reviewing the day-time chemistry.

Day-time tropospheric chemistry

The first Environmental Brief (1) considered in detail the photolysis of ozone at near-ultraviolet wavelengths to generate electronically excited oxygen atoms:



Reaction R1 is a key process in tropospheric chemistry because the $\text{O}({}^1\text{D})$ atom has sufficient excitation energy to react with water vapour to produce hydroxyl radicals:



Reaction with oxidants such as OH is typically the rate determining step for removing trace gases from the atmosphere. Almost all gases emitted into the atmosphere derive from processes occurring at the Earth's surface (e.g. natural emissions from biota on land or in the oceans; anthropogenic emissions from agriculture or from fossil fuel combustion for energy generation, industry and transport). Thus gases enter the atmosphere "from the bottom", where they also encounter the OH radical. Only the few gases that are unreactive towards OH radicals (e.g. chlorofluorocarbons) persist long enough in the troposphere to be transported up to the stratosphere.

The chemistry of OH is inextricably linked to the chemistry of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$). Reactions of OH with atmospheric trace gases usually produce hydroperoxy radicals, HO_2 , which are recycled back to OH by reaction with NO. In the process, NO is oxidised to NO_2 . The latter photolyses to produce ground-state oxygen atoms, $\text{O}({}^3\text{P})$, that recombine with molecular oxygen to produce ozone. Tropospheric ozone is a harmful air pollutant and a greenhouse gas.



Night-time tropospheric chemistry

It is an obvious statement: there is no sunlight at night. Therefore the night-time concentration of OH is (almost) zero. Instead, another oxidant, the nitrate radical, NO_3 , is generated at night by the reaction of NO_2 with ozone. NO_3 radicals further react with NO_2 to establish a chemical equilibrium with N_2O_5 .



Reaction R6 happens during the day too. However, NO_3 is quickly photolysed by daylight, and therefore NO_3 and its equilibrium partner N_2O_5 are both heavily suppressed during the day.

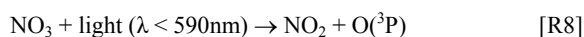


Figure 1 provides an overview of night-time chemistry. It is worth noting that night-time chemistry could not exist in isolation from day-time chemistry: reaction R6 needs ozone to oxidise NO_2 to NO_3 , and ozone is a product of day-time photochemistry. The chemistries of the two most important night-time species, NO_3 and N_2O_5 , are discussed below. For readers wishing to know more detail, I recommend a recent review of night-time chemistry by Brown and Stutz (2).

NO_3 chemistry

The night-time oxidant, NO_3 , is less reactive than its day-time counterpart, OH. For example, OH reacts with volatile organic compounds (VOC) by abstracting a hydrogen atom. NO_3 generally does not perform hydrogen abstraction reactions, although there are some notable exceptions: the $\text{NO}_3 + \text{CH}_3\text{SCH}_3$ reaction is an efficient sink for the dimethyl sulphide emitted by plankton in the surface ocean, and is a

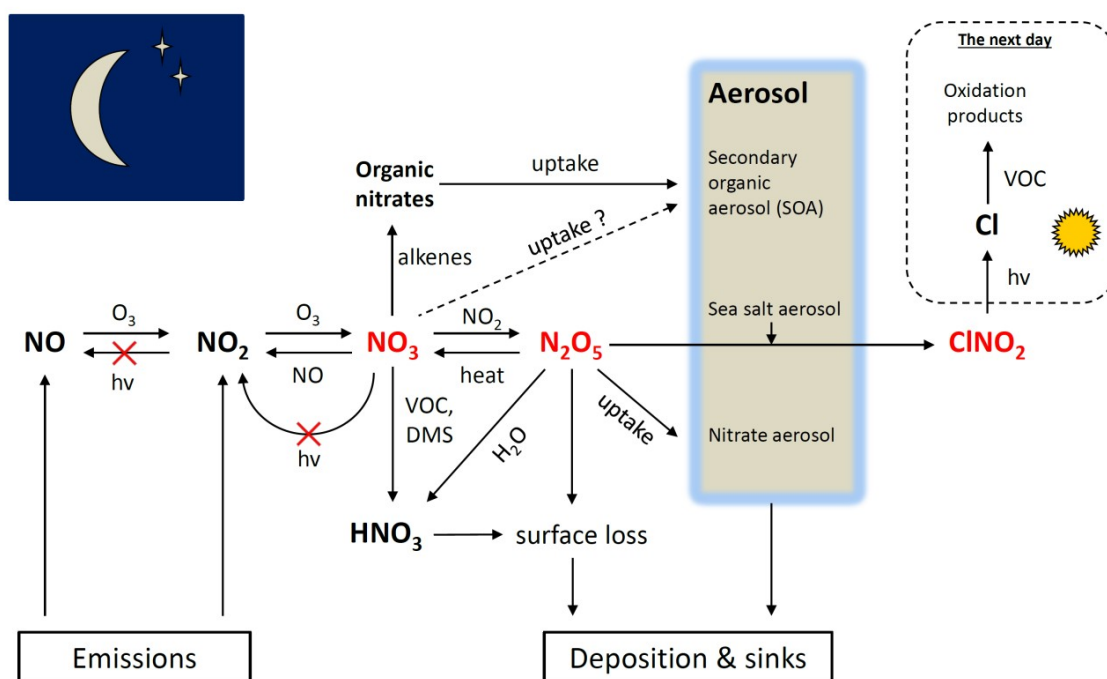


Figure 1: An overview of the chemistry in the troposphere at night. The species coloured in red are generated only at night. DMS = dimethyl sulphide; hv represents a photon of light.

route to produce sulphate aerosol around which marine cloud droplets can nucleate.

Instead, NO_3 more usually reacts with carbon-carbon double bonds; this reaction is also available to OH. Indeed OH reacts faster with double bonds than NO_3 but, crucially, because atmospheric concentrations of NO_3 at night are typically two orders of magnitude greater than day-time OH concentrations, the amounts of unsaturated VOCs oxidised by NO_3 are comparable to, and sometimes exceed, the amounts oxidised by OH. NO_3 reacts particularly rapidly with isoprene and terpenoid compounds emitted by plants, for which NO_3 is often their dominant sink. An important difference is that the radical chain reactions subsequent to the initial OH + VOC reaction recycle OH to react again (R3), whereas NO_3 + VOC reactions are usually stoichiometric in NO_3 . The addition of NO_3 to double bonds generates nitrate-substituted peroxy radicals, some of which react/decompose to generate HO_2 radicals; it is thought that reaction of this HO_2 with NO (R3) could generate low levels of OH at night, potentially propagating the oxidation of compounds that do not themselves react with NO_3 . The non-radical oxidation products of NO_3 + VOC reactions are multi-functional organic nitrates containing alcohol, peroxide or carbonyl groups. These compounds have low vapour pressures and consequently partition onto atmospheric particles to generate secondary organic aerosol (SOA) which is an air pollutant. Laboratory experiments have found higher SOA yields from NO_3 + VOC reactions than the correspond-

ing OH reactions. Laboratory studies also suggest that NO_3 radicals react directly with organic components in aerosol particles.

N_2O_5 chemistry

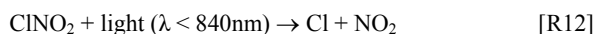
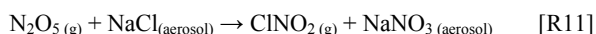
Much of the atmospheric chemistry of N_2O_5 occurs on the surfaces of, or inside, aerosol particles. N_2O_5 is readily taken up by aqueous inorganic particles and water droplets, where it undergoes hydrolysis with liquid water to produce nitric acid. The latter is then often neutralised by the uptake of ammonia.



Reactions R9 and R10 and the subsequent deposition of nitrate aerosol to the surface is one of the few mechanisms by which NO_x is removed from the atmosphere. This nighttime sink can remove as much NO_x as the day-time gas-phase reaction of OH with NO_2 to produce nitric acid. Night-time loss of N_2O_5 limits the availability of NO_2 for the photochemical production of ozone the following day *via* reactions R4 and R5 (3).

Another intriguing aspect of the heterogeneous chemistry of N_2O_5 is its reaction with chloride ions in sea salt aerosol to produce nitryl chloride. ClNO_2 is stable at night, but is photolysed within approximately 1 hour of sunrise the next

morning. Photolysis liberates chlorine atoms which react with VOCs.



Via the above chemistry, night-time processes enhance the VOC oxidation chemistry occurring the next morning (4). Interestingly, the NO_2 co-product of photolysis R12 remains available to contribute to photochemical ozone production, circumventing the usual process by which N_2O_5 uptake onto aerosol removes NO_x from the atmosphere. Chlorine atoms are more reactive than NO_3 radicals (and more reactive than OH), and so chlorine activation leads to the oxidation of VOCs that do not react with NO_3 directly. Chlorine atom-initiated oxidation of methane R13 has been proposed as an additional minor sink constraining the atmospheric lifetime of this important greenhouse gas.

Measurement of NO_3 and N_2O_5

In large part, the substantial improvements made over the last decade to our understanding of night-time chemical processes are due to the advent of new measurement techniques able to quantify concentrations of NO_3 and N_2O_5 *in situ*. Before these techniques, the first measurements of ambient NO_3 reported in the late 1970s and early 1980s used differential optical absorption spectroscopy (DOAS) at red visible wavelengths. The very low concentrations of ambient NO_3 required that the absorption measurements be conducted over long light paths through the atmosphere (several kilometres), resulting in an inherent spatial averaging of the NO_3 concentrations measured along the light path, and consequent difficulties in interpreting the observations. The absorption spectrum of N_2O_5 does not have absorption features at any convenient wavelengths, so such instruments could not detect N_2O_5 . Instead N_2O_5 concentrations had to be inferred from NO_3 and NO_2 measurements by applying the (then untested) assumption that these species were in equilibrium, R7.

The first *in situ* “point measurements” of NO_3 were made by electron spin resonance (ESR). However, nowadays most instrumentation uses variants of cavity ring-down spectroscopy (CRDS) and cavity enhanced absorption spectroscopy (CEAS) (5, 6). These methods use many reflections of the probe light beam to achieve multi-kilometre absorption paths through gas samples held inside a high finesse optical cavity. At ground level, and especially if pollution sources are nearby, NO_3 concentrations are suppressed by the fast reaction of NO_3 with NO, the latter being a component of fresh emissions from fossil fuel combustion. Because CRDS and CEAS instruments can be made relatively compact, they have been flown on aircraft (3) and deployed from tall buildings (6) to measure NO_3 concentrations well above the

ground. These measurements showed substantial NO_3 concentrations are present away from the surface, indicating that night-time chemistry is more active than previously thought based on ground-based DOAS measurements, and confirming some intriguing earlier DOAS measurements of NO_3 in the free troposphere that suggested large concentrations of NO_3 could exist aloft (7).

CRDS and CEAS instruments also enabled N_2O_5 to be measured for the first time by drawing ambient air through a heated inlet to thermally dissociate N_2O_5 and measuring the extra NO_3 signal (5). These measurements demonstrated that NO_3 and N_2O_5 are in equilibrium, or at least close to equilibrium, in most regions of the atmosphere. There is also generally sufficient NO_2 to drive the equilibrium in favour of N_2O_5 .

References

1. M. King, ‘Calculating photolysis rates and estimating photolysis lifetimes’ (*ECG Environmental Brief No 1*), *ECG Bulletin*, July 2013, p 21.
2. S. S. Brown and J. Stutz, ‘Night-time radical observations and chemistry’. *Chem. Soc. Rev.*, **41**, 6405–6447, 2012; doi: 10.1039/c2cs35181a.
3. S. S. Brown *et al.*, ‘Variability in nocturnal nitrogen oxide processing and its role in regional air quality’. *Science*, **311**, 67–70, 2006; doi: 10.1126/science.1120120.
4. J. A. Thornton *et al.*, ‘A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry’. *Nature*, **464**, 271–274, 2010; doi:10.1038/nature08905.
5. S. S. Brown, H. Stark, S. J. Ciciora, and A. R. Ravishankara, ‘*In situ* measurement of atmospheric NO_3 and N_2O_5 via cavity ring-down spectroscopy’. *Geophys. Res. Lett.*, **28**, 3227–3230, 2001; doi: 10.1029/2001GL013303.
6. A. K. Benton *et al.*, ‘Night-time chemistry above London: measurements of NO_3 and N_2O_5 from the BT Tower’. *Atmos. Chem. Phys.*, **10**, 9781–9795, 2010; doi: 10.5194/acp-10-9781-2010.
7. S. R. Aliwell and R. L. Jones, ‘Measurements of tropospheric NO_3 at mid-latitude’. *J. Geophys. Res. (Atmospheres)*, **103**, 5719–5727, 1998.

Dr STEPHEN BALL

Department of Chemistry,
University of Leicester

ECG Environmental Briefs

Atmospheric particulate matter

(ECGEB No 4)

Atmospheric particulate matter is a central component of the atmospheric chemical and climate system, a major air pollutant harmful to human health, and a component of biological systems and global biogeochemical cycles

The terms particulate matter (PM) or aerosol particles describe condensed (solid or liquid) material suspended in the atmosphere. They include crustal material, soot, combustion particles, nucleating clusters and biological material such as spores, but not by convention raindrops, hail or other hydrometeors. The term aerosol is often used in reference to PM, but technically refers to both the condensed phase particles and the gaseous medium they are suspended in. Primary PM is released to the atmosphere from sources such as incomplete combustion, dust and sea salt. Secondary PM is formed in the atmosphere from the condensation of low volatility gases such as sulfuric acid, ammonia and functionalised organic compounds. Many airborne particles comprise both anthropogenic and natural components.

Physical properties of PM

Size: Atmospheric particles have a range of shapes and morphologies. Their size is a somewhat elusive property; a number of operationally defined metrics are used, perhaps most commonly aerodynamic diameter. A particle with an aerodynamic diameter of 1 μm will exhibit the same inertial properties as a sphere with a diameter of 1 μm and a density of 1 g cm^{-3} , irrespective of the actual size, shape or density of the particle. A trimodal size distribution is commonly observed in the lower atmosphere, with a nucleation mode ($< 0.1 \mu\text{m}$ diameter), an accumulation mode (~ 0.1 to $2 \mu\text{m}$), and a coarse mode ($> 2 \mu\text{m}$). Secondary particles are formed in the nucleation mode (or, more commonly, material condenses onto existing particles). Particles grow in the accumulation mode through coagulation and condensation. Mechanically generated primary particles are mostly emitted in the coarse mode. The lifetime of accumulation-mode particles is largely determined by precipitation, whereas nucleation-mode particles more readily diffuse and undergo agglomeration, and the largest coarse mode particles undergo gravitational settling at appreciable rates. The greatest numbers of particles are in the nucleation mode; the greatest mass is in the coarse mode.

Composition: Typical continental urban boundary layer PM samples include natural crustal materials (carbonates, silicates), inorganic constituents such as sulfate (SO_4^{2-}), nitrate (NO_3^-), sodium, potassium, chloride and ammonium (NH_4^+), trace quantities of group I and II metals and other species

such as copper, arsenic, zinc and vanadium (found in fuels and derived from crustal sources and vehicle brake and tyre wear), and organic components. The latter include products of incomplete combustion (such as soot or black carbon), larger molecules such as polycyclic aromatic hydrocarbons (PAHs) and secondary organic aerosol (SOA), formed from oxidation and subsequent condensation of volatile organic compounds (VOCs). Sea salt is an important contributor of sodium, chlorine and other ionic components; sulfate and nitrate originate in sulfuric and nitric acid, which in turn are derived from the gas-phase oxidation of SO_2 and NO_x respectively. Ammonia, derived mainly from agriculture, readily dissolves in aqueous particles and neutralises sulfate and nitrate, which are usually found as ammonium sulfate or ammonium nitrate in urban regions.

Abundance: Most current legislative limits to PM abundance, developed from an air quality perspective, relate to mass concentration below a certain size limit—commonly PM_{10} and $\text{PM}_{2.5}$, denoting the concentration of PM with aerodynamic diameters below ca. 10 and 2.5 μm respectively, which correspond roughly to adult human inhalable (thoracic) and respirable (alveolar) particle sizes respectively. Typical urban atmospheric loadings of PM range from tens to hundreds of $\mu\text{g m}^{-3}$ for PM_{10} . For a city such as London, a mean mass concentration for PM_{10} of the order of $30 \mu\text{g m}^{-3}$ might be observed; considering the area of Greater London (ca. 400 km^2) and assuming a 1 km boundary layer height, this equates to around 12 tonnes of material suspended above the city.

Importance and impacts of PM

Human health impacts: Particulate matter has been a dominant factor in historical air pollution episodes, including the London Smogs of the 1950s and the Donora Valley (Pennsylvania) and Meuse Valley (Belgium) episodes. Inhalation of PM in an urban atmospheric context is associated with enhanced respiratory and cardiovascular disease (marked by an increase in hospital admissions) and increased associated mortality. The figures are not trivial: studies find a 1 to 4 % increase in cardiovascular mortality per $10 \mu\text{g m}^{-3}$ increase in PM_{10} (1). In the UK, eliminating all anthropogenic $\text{PM}_{2.5}$ (a practical impossibility) would increase life expectancy from birth by approximately six

months, averaged across the whole population—roughly double the impact from elimination of all road accidents or passive smoking (2). Those with pre-existing respiratory conditions, as well as the young and elderly are at greater risk. PM mass concentrations in many nations are substantially higher than those in the UK, particularly in the developing world; burning wood, coal or biomass for domestic heating and cooking is a substantial source of personal exposure to PM in many such areas.

Impacts on climate and atmosphere: Atmospheric PM loading contributes to the reduction in visibility associated with poor air quality, and both directly and indirectly affects atmospheric radiation transmission and hence climate. These effects (mainly but not exclusively cooling in nature) are among the largest, and least well quantified, terms in climate models and could potentially substantially alter the magnitude of the calculated warming (3). Aerosol particles also play important roles in atmospheric chemistry, providing a reaction site for heterogeneous reactions that would not otherwise occur. Dust transport is an important component of the biogeochemical cycles for crustal minerals, notably iron, representing a major route for their input into marine ecosystems. Recently, the role of bioaerosols (viruses, fungal spores, plant and animal debris) has received increasing attention because of their potential role as cloud and ice nuclei and their health impacts, particularly allergenic reactions.

Legislative measures

Table 1: Air Quality Standards for Particulate Matter

	WHO guidelines (4)	EU Standards
PM₁₀	20 $\mu\text{g m}^{-3}$ (annual mean)	40 $\mu\text{g m}^{-3}$ (annual mean)
	50 $\mu\text{g m}^{-3}$ (24hr average)	50 $\mu\text{g m}^{-3}$ (24 hr average, < 35 exceedances / yr)
PM_{2.5}	10 $\mu\text{g m}^{-3}$ (annual mean)	25 $\mu\text{g m}^{-3}$ (annual mean) Target Value from 2010; Limit Value from 2015. See AEI discussion in text
	25 $\mu\text{g m}^{-3}$ (24hr average)	

Air Quality Standards for protection of health are set by bodies such as the World Health Organisation (WHO) and EU (Table 1). EU member states will have to meet an objective of 25 $\mu\text{g m}^{-3}$ for all annual average PM_{2.5} levels by 2015; this value has been an aspirational target value since 2010. Average Exposure Index (AEI) limits will also soon come into force. The AEI is the three-year running mean of PM_{2.5} levels in urban background locations; PM_{2.5} exposure reduction targets, for AEIs relative to levels measured over the period 2009–2011, will come into force by 2020. The

aim of the AEI concept is to reduce population-level exposure to PM_{2.5}, rather than focussing on the most polluted locations. The EU Thematic Strategy on Air Pollution, which drives the EU directives from which national environmental legislation is derived, is currently under review.

Compliance: In the UK, all areas meet current annual mean limit values for PM₁₀ and PM_{2.5}, although the PM₁₀ 24-hour target has been exceeded in Central London. Further policy measures are likely to be required to meet future PM_{2.5} exposure reduction targets. Worldwide, the situation is very different. Unlike long-lived greenhouse gases, which are globally mixed, the health effects of PM are usually felt locally to the emission region, and so should be more amenable to national policy initiatives. Tensions exist between climate (“carbon”) policy and air quality; for example, increased use of local biofuel combustion for combined heat and power may increase local PM levels, and higher-mileage (lower-carbon) diesel vehicles are associated with higher primary and secondary PM formation. Yet globally, aerosol particles (other than black carbon) offset a substantial fraction of the warming that would otherwise result from greenhouse gases. Wider appreciation of the health impacts of PM exposure will inform development and acceptance of the optimum policy response.

Links and resources

- EU Air Quality Objectives: <http://ec.europa.eu/environment/air/quality/standards.htm>
- UK Air Information Resource: <http://uk-air.defra.gov.uk>

References

1. R. L. Maynard, ‘Health effects of urban pollution’. In *Air Quality in Urban Environments. (Issues in Environmental Science and Technology, Vol. 28)*, R. E. Hester and R. M. Harrison, Eds., Royal Society of Chemistry, Cambridge, 2009, pp 108–128.
2. *The Mortality Effects of Long-Term Exposure to Particulate Air Pollution in the UK*; Committee on the Medical Effects of Air Pollutants (COMEAP), 2010.
3. S. Solomon, *et al.*, *Climate Change: The Physical Science Basis, IPCC Fourth Assessment Report*, Cambridge University Press, 2007.
4. WHO (2006), *WHO Air Quality Guidelines: Global Update 2005*, WHO/SDE/PHE/OEH/06.02 (2006); http://www.euro.who.int/__data/assets/pdf_file/0005/78638/E90038.pdf

Dr WILLIAM BLOSS

School of Geography, Earth and Environmental Sciences,
University of Birmingham,
w.j.bloss@bham.ac.uk

RSC Green Chemistry Series – New title

Element Recovery and Sustainability

Element Recovery and Sustainability

Royal Society of Chemistry, Cambridge, 2013

Editor: Andrew Hunt ISSN: 1757-7039

Price: £149.99

Increasing consumption and the development of new low carbon and electronic technologies are broadening concerns over future elemental sustainability for a wide range of elements from phosphorous to indium. This issue is rapidly rising up the political, economic and research agendas and this book will tap into this interest to highlight and discuss the problem and current ideas, research and innovation to increase elemental recovery. It covers a multi-disciplinary blend of knowledge from the chemistry, engineering and biotechnology sectors ranging from ionic liquid recovery methods to hyperaccumulation in plants. The editors have a strong background in the utilisation of waste, green chemistry technologies and utilisation of bio-derived resources, and this is the first book to look at the overall issue, providing a new perspective through drawing together many different techniques for researchers and policy makers.

CONTENTS

- Elemental sustainability and the importance of scarce element recovery
- Integration of traditional methods for elemental recovery in a zero-waste recycling flow sheet
- Ionometallurgy (ionic liquids in metallurgy)
- Biosorption of elements
- Hyperaccumulation by plants
- Anthropospheric losses of platinum-group elements
- *f*-Block elements recovery
- WEEE waste recovery
- Mining municipal waste: prospective for elemental recovery

From the Preface

The 21st century has seen a growing recognition of the importance of resource management including the more careful use of resources, an awareness of their lifecycles and a move towards a more closed-loop approach to manufacturing. In the context of sustainable chemistry, while the 1990s saw the emergence of the green chemistry movement, with a strong focus on clean production and waste minimization in manufacturing, the new century has seen a move towards a much more holistic view. While clean and efficient manufacturing remains key and arguably the cornerstone of chemical sustainability, we now understand that this must be accompanied by a greater use of renewable resources as well as shift to environmentally compatible products. The emphasis to date in renewable resources has been on carbon – we have all become familiar with the challenges of declining traditional fossil feedstocks and the need for a smaller carbon footprint, yet only now are concerns over other elements and elemental cycles being taken seriously. Society uses a very large number of the elements in its everyday activities. Carbon, nitrogen, oxygen, hydrogen and phosphorus, in particular, are fundamental and commonplace in life. Others including iron, chlorine, bromine, selenium and potassium are also vital to natural processes if perhaps less widely appreciated. In addition to these we have chosen to build a society around many other elements – nickel, tungsten, chromium, copper and vanadium alongside boron, gold, silver, palladium, platinum and many others are found in a multitude of articles from buildings to electronics and from sophisticated equipment to complex drug molecules. Ironically, the move to a low-carbon economy – a laudable goal in principle, if not in practice – has made the problem worse by consuming large amounts of main group and rare earth elements, that are not normally used to any great extent, in batteries, wind turbines, hybrid cars and other increasingly popular alternative, low-carbon technologies. We know where these elements occur and we know a lot about their chemistries (entire book series have been written about some of them), yet we know very little about their elemental cycles which, given our almost obsessive interest in carbon cycles, seems surprising. How does our use of fluorine for example, in an increasingly high proportion of pharmaceuticals, agrochemicals and electronic chemicals affect the natural lifecycle of fluorine (which includes large quantities of static minerals

and frequent emissions of hydrogen fluoride from volcanoes)? We are very aware of the dangers of halocarbons and compounds such as sulfur hexafluoride in the atmosphere but what about less volatile organofluorine molecules in the terra-sphere? The importance of achieving a better understanding of the elements in terms of their use, recovery and interaction with the environment is discussed in Chapter 1 and at various other stages in the book, in particular in Chapter 7 where the special case of platinum group metals – with applications from the decorous (jewellery) to the essential (catalysts for emission control and for the manufacture of pharmaceuticals) are discussed in terms of anthropospheric losses. The book also focuses on both tradition and novel methods of metal recovery (Chapters 2 and 3).

If we can learn to recover elements from waste, if we can process more efficiently and if we can design articles (or processes) better so that they use less critical elements and enable recovery of those elements when the article (or process) reaches its end of life, then we are making massive steps towards elemental sustainability even in resource-deficient regions such as western Europe.

The use of benign and more efficient processes and the recovery of otherwise wasted or lost valuable elements are described in Chapters 4, 5, 6, 8 and 9. These cover bio- and non bioprocesses and also look at metals and non-metals. They include a chapter on the especially important challenge and opportunity for WEEE mining, the enormous amount of waste electronics we produce each year, which is growing at a staggering rate – surely we cannot continue to treat our slightly out-of-date phone, television and other devices which such lack of respect for the elements that went into them. This balance in favour of practical technologies is deliberate: politicians can and do spend long hours debating these issues but as scientists we have a responsibility to develop practical solutions and these must include effective ways of recovering valuable elements both to reduce environmental harm and to recover and re-use the precious and limited resources our planet gives us. To put the words of Mahatma Gandhi into a modern consumer society context: “. . .we can satisfy all of our needs if we are resource intelligent”.

James Clark – University of York, UK, **RSC Green Chemistry Series** Editor in Chief

Forthcoming symposium: Organic chemistry and toxicity of contaminants in the ground

Where: Chemistry Centre, Burlington House, London, UK When: Thursday, 13th February 2014

This meeting is focussed on exploring the chemistry and toxicity of Contaminants of Emerging Concern (emerging contaminants) which are those that have recently been discovered in soil and water environments and are considered to be a potential risk to the environment and/or human health. The meeting will also explore “common historic contaminants” in the ground that are generally recognised as a risk to human health and/or the environment. These contaminants are present in the environment generally due to a historic lack of regulation, poor use, storage practices and waste disposal and are subject to remediation.

Topics and speakers include:

- Reaction mechanisms and the Environmental Fate Simulator – Eric Weber, US EPA
- Emerging contaminants in the ground – Marianne Stuart, British Geological Survey
- Human exposure, body burdens and health effects of PFOA and PFOS – Tony Fletcher, LSHTM
- Fractionating hydrocarbons for hazard and risk assessment; chemical and biological analysis – Graeme Paton, University of Aberdeen.

On-line registration (£60 for RSC members, £30 student or retired RSC members, £90 non-members) is available at: <https://events.rsc.org/rsc/frontend/reg/fhome.csp?eventID=258>

We welcome abstracts for poster presentation during the breaks for this meeting. Please send a brief abstract (~250 words) to kate.jones@hsl.gsi.gov.uk by Friday 10th January 2014 for consideration.

This event has been organised by James Lymer and Kate Jones on behalf of the **Environmental Chemistry and Toxicology Groups**. The event is also supported by the **RSC Environment, Sustainability and Energy Division**.