Royal Society of Chemistry Environmental Chemistry Group
(www.rsc.org/ecg)

July 2015

ECG *Bulletin*

Emerging contaminants. James Lymer *et al.* (pp. 8-10) report on a meeting on emerging contaminants in waters and soils. The theme is taken up by David Megson *et al.* (pp. 19-22), who review how non-targeted methods can detect new and emerging persistent environmental pollutants.

Peroxy radicals. In our latest ECG Environmental Brief, John Orlando (pp. 23-24) outlines the atmospheric chemistry of hydroperoxyl and organic peroxy radicals.

Also in the issue. Zoë Fleming answers our questions in the ECG Interview (p. 6) and reviews a recently published RSC book, ‘Geoengineering of the Climate System’ (p. 18). We explore the environmental impacts of neonicotinoid pesticides (pp. 3-4). James Lymer (p. 5) discusses the implications of an updated assessment of suitable levels of contaminants in soils published earlier this year. We also publish reports from recent meetings organised by the ECG.

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***Cover image:** Water treatment plant at sunrise. Credit: Chaiyapruk Chanwatthana/Shutterstock*

ECG *Bulletin*

ISSN 1758-6224 (Print) 2040-1469 (Online)

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

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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 Prizmatic Print Solutions, www.prizmatic.co.uk; 01444 239000.

Update

How harmful are neonicotinoids to the environment?

The World Integrated Assessment of the Impacts of Systemic Pesticides on Biodiversity and Ecosystems (WIA), published on 9 January 2015 (1), provides a synthesis of existing research on the environmental impacts of neonicotinoid pesticides and fipronil, a pesticide with similar properties. Based on over 800 published studies, the report concludes that "the wide-scale use of these persistent, water-soluble chemicals is having widespread, chronic impacts upon global biodiversity." A recent report by the European Academies Science Advisory Council comes to similar conclusions (2).

Neonicotinoids were first discovered in the 1990s and have since become the most widely used class of insecticides (**Figure 1**). They are less toxic to vertebrates than to invertebrates and can be applied as seed treatments, soil treatments, and foliar sprays. Neonicotinoids become distributed throughout the plant (they are systemic), making them very effective against sucking pests. They are also used in livestock, aquaculture, and domestic animals. However, studies have shown that many non-target species, particularly bees, are also affected by neonicotinoids. These concerns have led to a partial, two-year ban on the use of neonicotinoids in the EU, starting on 1 December 2013 (3). The recently published European Red List of Bees points to pesticides as one of main threats to bee species, 9.2% of which are classified as at threat of extinction (4). The WIA provides an overview of existing research on the effects of neonicotinoids and another systemic pesticide, fipronil. In this ECG *Bulletin* article, the term 'neonicotinoid' covers both fipronil and the neonicotinoids.

In a series of papers in reference (1), the WIA presents evidence of the extensive use of neonicotinoids worldwide and the persistence of these pesticides and their metabolites in the environment. The effects on non-target invertebrates and on vertebrates, and the resulting risks to ecosystem function, are discussed. Another article in the same issue presents alternatives to neonicotinoid use for combating maize pests and ash borer infestations.

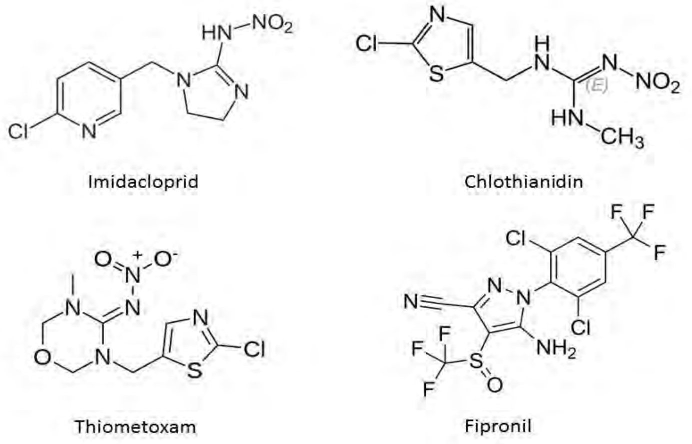

Imidacloprid
Chlothianidin
Thiometoxam
Fipronil

Figure 1. Neonicotinoids and fipronil. *The neonicotinoid midacloprid is the most commonly used pesticide in the world today. Thiometoxam and chlothianidin are other examples of widely used neonicotinoids. Fipronil acts in a different way but is also systemic,* i.e. *it is distributed throughout the plant.*

Determining how harmful neonicotinoids are to the environment turns out to be complicated, but three things stand out. First, neonicotinoid use has increased rapidly around the world over the past two decades despite limited evidence that it increases yields or is cost-effective – and indeed, some evidence that it is not (5). Secondly, much of this use, particularly in seed treatments, is prophylactic, resulting in widespread, continuous exposure of both target and non-target species to low concentrations of these pesticides. Such prophylactic use is not compatible with integrated pest management, an approach that has been compulsory for all crops in the EU since 1st January 2014 (6). And thirdly, both the approval process and existing toxicology testing regimes are wholly inadequate for these pesticides, neglecting both their widespread sub-lethal effects on numerous non-target species and synergistic effects resulting from exposure to more than one pesticide or to other additional stressors. For most non-target insect and other invertebrate species that are likely to be exposed to neonicotinoids, "no or very little information is available about the impact of these pesticides on their biology" [reference 1, p. 69]. Furthermore, many effects are highly variable, depending not only on the species but also on the age of the individual, how long it has been exposed, and many other factors.

There are cases when neonicotinoids are clearly toxic to non-target species. For example, some bee deaths have been attributed convincingly to neonicotinoid-laden dust after planting. But many other possible effects are more subtle, and observations are difficult to attribute to a specific cause. Pesticide concentrations in pollen or nectar may be on the order of parts per billion, requiring extremely sensitive measurement techniques for detection. Effects may be cumulative over time and may differ between species or, in the case of bees, between different members of the society. Studies have shown that neonicotinoid exposure at levels well below that causing mortality can affect bees' ability to return to the colony (7); reduce burrowing ability of earthworms (8); and cause paralysis and impaired walking in beetles (9). But it is very difficult to prove these effects at field-realistic conditions (**Figure 2**). A recent field study (10) makes an important step in this direction by investigating the impact of neonicotinoid exposure on both honey bees and wild bees near oilseed rape fields treated with neonicotinoid. The study is the largest field study so far, involving eight treated fields and eight control fields. In treated fields, the authors found fewer solitary wild bees and a reduced bumblebee colony growth rate.

Overall, the body of evidence presented in the assessment gives clear reasons for concern. Hallmann *et al.* have reported that declines in insect-eating birds in the Netherlands correlate with neonicotinoid use (11), showing the potential cascading effects of these pesticides. It may not be straightforward to implement alternatives, particularly in large-scale agriculture. But continuing to use neonicotinoids at current levels carries the risk of serious environmental damage (12), particularly to non-target species that have important ecosystem functions, such as bees and earthworms, with potentially serious implications for food security.

The ECG Bulletin Editors

Figure 2. *Small corn plants at sunrise. Maize seeds are often treated with neonicotinoids before planting. Credit: Paul Gerritsen/Shutterstock*

References

1. WIA, special issue, *Environ. Sci. Pollut. Res.* **22**, Issue 1, pp. 1-154 (2015).
2. Ecosystem services, Agriculture, and Neonicotinoids, EASAC policy report 26, April 2015, available at www.easac.eu.
3. Regulation (EU) No. 485/2013, see http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:32013R0485
4. A. Nieto *et al.*, European Red List of Bees (Publication Office of the European Union, Luxembourg, 2014).
5. L. Furlan, D. Kreutzweiser, "*Environ. Sci. Pollut. Res.* **22**, 135-147 (2014).
6. Directive 2009/128/EC, see http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2009:309:0071:0086:en:PDF.
7. M. Henry *et al.*, *Science* **336**, 348-350 (2012).
8. N. Dittbrenner, I. Moser, R. Triebskorn, Y. Capowiez, *Chemosphere* **84**, 1349-1355 (2011).
9. B. A. Kunkel, D. W. Held, D. A. Potter, *J. Econ. Entomol.* **94**, 60-67 (2001).
10. M. Rundlöf *et al.*, *Nature* **521**, 77-80 (2015).
11. C. A. Hallmann, R. P. B. Foppen, C. A. M. van Turnhout, H. de Kroon, E. Jongejans, *Nature* **511**, 341-343 (2014).
12. F. Sanchez-Bayo, *Science* **346**, 806-807 (2014).

Update

Human health exposure from contaminated land: A LQM/CIEH report

James Lymer (Wardell Armstrong LLP)

Since 2002, the Environment Agency has used the Contaminated Land Exposure Assessment (CLEA) model to determine soil guideline values, which are soil concentrations that represent a minimal risk to human health (1). A recent report by Land Quality Management (LQM) and the Chartered Institute for Environmental Health (CIEH) provides an updated assessment of suitable for use levels in soils (S4ULs) for 89 substances (2).

LQM/CIEH previously published two editions of Generic Assessment Criteria (GAC) in 2006 and 2009, respectively. These GAC complemented the available SGVs produced by the Environment Agency (EA) from 2002 onwards. Few Soil Guideline Values (SGVs) have been produced by the EA and there is little indication that further values will be published in the near future. Since the 2009 edition of the LQM/CIEH GAC report, several changes have occurred in the contaminated land risk assessment sector. First, various revised values for exposure, toxicology and physicochemical parameters have been adopted in the UK. Secondly, in December 2013, DEFRA produced Category 4 Screening Levels (C4SL) for assessment of land affected by contamination (3). This approach included new exposure land uses for public open space, suggested modifications to the exposure parameters, and set the toxicity value at low risk rather than the minimal risk adopted in the derivation of other GACs.

Considering the above developments, LQM/CIEH published a report on *Suitable 4 Use Levels* in January 2015 (2). An S4UL is a soil concentration that represents a minimal risk to long term human health. The methodology for deriving the S4ULs is based on a modified version of the Environment Agency CLEA model (1). The S4ULs were derived using an iterative approach including modification of the exposure parameters in the CLEA model. The toxicology input (health criteria values) is an estimated contaminant concentration that would pose a tolerable or minimal risk to human health and is a lower level of risk than that used to derive C4SLs. The health criteria values were selected in accordance with Environment Agency guidance (1), which was used in the derivation of previous GACs and the SGVs. The S4UL derivation included updated contaminant toxicology input values, fate and transport properties and exposure parameters, such as the vapour inhalation rate as updated by the United States Protection Agency in 2011. The report includes suitable-for-use levels (S4UL, a type of GAC) for 89 substances including metals, total petroleum hydrocarbon fractions (aromatic and aliphatic), polycyclic aromatic hydrocarbons, and chlorinated hydrocarbons. The S4UL values were derived for six generic land uses: residential with and without home-grown produce, commercial, allotments, and public open space as parks and as land adjacent to residential dwellings.

For example, benzo[*a*]pyrene is a proven human carcinogen and is classed as a non-threshold contaminant. To obtain the S4UL, the CLEA model is used to estimate the average daily exposure from benzo[*a*]pyrene in soil, which is equivalent to its toxicity value. This is reported as a soil concentration that represents a minimal risk to long term human health, that is, a S4UL. Further details on the derivation and application of these assessment criteria are presented in (2) and in the CLEA framework reports.

References

1. Environment Agency, CLEA Reports, see https://www.gov.uk/government/collections/land-contamination-technical-guidance
2. LQM/CIEH, 'Suitable 4 Use Levels' http://www.lqm.co.uk/publications/
3. DEFRA, SP1010 – Development of Category 4 Screening Levels for assessment of land affected by contamination, updated in September 2014.

Previous ECG *Bulletin* articles on contaminated land may be found in the July 2008 (pp. 18-20), January 2010 (p. 36) and July 2014 (p. 4 and p. 21) issues, see http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/bulletin.asp.

The ECG Interview: Dr. Zoë Fleming

ECG committee member and Honorary Secretary Dr. Zoë Fleming is a research scientist with the National Centre for Atmospheric Science (NCAS), based at the University of Leicester. Here she tells us about her career as an environmental chemist.

What inspired you to become a scientist? As a child, there was so much about nature that I found intriguing and wanted to find out more about. I was interested in how all the systems on the Earth are interlinked. I was good at math at school but didn't see how it applied to the real world, and it only started to make sense when we used numbers and equations to explain natural phenomena in science lessons. When I was 15, I heard about James Lovelock's Gaia hypothesis in a biology class and something suddenly clicked. I knew then that the link between chemistry and the Earth's climate was what I wanted to study.

How did you come to specialise in atmospheric chemistry? I didn't know right away what type of environmental chemistry I would go into. I started off in ecosystem pollution and then marine chemistry. What most fascinated me was how the ice core records provide a footprint of past interactions between land, sea and atmosphere. I then ended up taking continuous measurements of atmospheric chemistry, sampling *in situ*. The invisible pollution in the atmosphere felt like an area I wanted to find more about. As this pollution isn't something the public can directly see, we have to let them know what is going on.

Could you describe your current job? I carry out data analysis involving the concentrations of trace gases in the atmosphere over the last few decades and how these concentrations have changed over time and according to where the air masses have travelled. I also run a series of small sensors that get used locally and for outreach work. My colleagues are based around the country and there is a lot of teamwork, travelling and networking in the projects I am involved with.

What advice would you give to anyone considering a career in environmental chemistry? It is a friendly and welcoming area to work in. Most people working in this area have the common goal of wanting to clean up the environment and work out how humans can have a smaller negative impact on the natural world. Jobs are usually quite varied and challenging and it is great if you like being outdoors, doing field work. If you enjoy the links to policy or environmental legislation, there are always ways in which your expertise can be used to make a difference.

What are some of the challenges facing the environmental chemistry community? As the public and large corporations are becoming more environmentally aware, our advice is often sought, but interpreted differently in the profit-driven world. Businesses, policy-makers and politicians want a black and white answer but environmental solutions are not always as clear-cut. Our advice is not always taken in the way we intended. Some compromises end up out of our hands and we may feel like our advice and solutions are not taken as seriously as we would like.

What is the most rewarding aspect of your career so far? The field work that I have done has taken me to fabulous locations around the world and I have made many friends along the way. I also enjoy writing papers on general topics and explaining science to the public and to students.

If you weren't a scientist what would you do? I would work outdoors, either helping to protect wild places or being involved with mountain activities or expeditions. My childhood ambition was to be a writer for National Geographic; keeping that gold standard in photography and travel/exploration writing in mind keeps on inspiring me to stay curious and learn more about the environment.

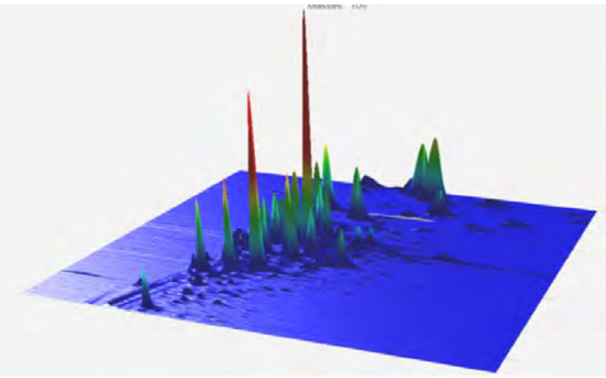
Meeting Report

The 6th International Multidimensional Chromatography Workshop

David Megson (Ryerson University and Ontario Ministry of the Environment and Climate Change; david.megson@ontario.ca)

On January 6th and 7th 2015, the 6th International Multidimensional Chromatography Workshop was held at the Ontario Ministry of the Environment and Climate Change (MOECC) in Toronto, showcasing advances in gas chromatography with applications in many areas, including environmental chemistry.

This event appears to be growing in popularity each year and attracted over 150 participants from industry, academia and government, with 32 speakers from around the globe, including Australia, Europe and North America. The meeting proved a great place to discuss recent advances in multidimensional chromatography and also see what new and diverse applications the technique is finding in the field of environmental chemistry.



Analysing complex mixtures. *This 3D chromatogram shows the complex mixture of phenolic compounds in a bio-oil sample.*

The first day contained a variety of interesting talks with several speakers explaining how to optimise analysis through the correct column combinations and modulation periods. There was also a tasty presentation by **Jeff Focant**, whose research group at the University of Liège, Belgium, has been analysing the composition of Trappist beers.

Several presentations focused on environmental chemistry applications, including the use of comprehensive two-dimensional gas chromatography (GCxGC) for characterising volatile organic carbons (VOCs) from diesel emissions (**Salim Alam**, University of Birmingham) and cadavers (**P-H Stefanuto**, University of Liege, Belgium); investigating debris from arsonous fires (**Phil Richards**, Chemistry Matters); and using GCxGC data processing scripts to identify emerging persistent organic pollutants (POPs) (**Miren Pena**, University of Toronto). It was great to see the large variety of different applications where multidimensional chromatography was being used to solve complex environmental problems.

My own presentation focused on identifying the source of polychlorinated biphenyl (PCB) exposure for workers at a transformer dismantling plant. I was originally scheduled to give my talk on the second day but took the opportunity to fill the slot of **John Dimandja** (Spelman College), the latest person to suffer the curse of Chicago O'Hare airport. The day ended with a social mixer in a local hotel which was kindly sponsored by Leco.

The second day included another set of high quality presentations. **Sarah Prebihalo** and **Maura McGonigal** (Penn State) discussed the use of GCxGC for environmental forensics investigations. Other speakers reported on the analysis of DDT derivatives in dolphins (**Susan Mackintosh**, San Diego State), exhaled breath condensate ((**John Dimandja**, Spelman College), and PACs in snow deposits (**Carlos Manzano**, Environment Canada). It was quite a shock to see the high levels of DDT and its derivatives that have been recorded in dolphins from the south west coast of the USA.

Whilst the conference was mainly focused on gas chromatography, there were also talks on multidimensional liquid chromatography (LC) and an interesting combination of LC with gene receptor assays for the simultaneous detection of chemicals and their toxicity (**Willem Jonker**, IVM-VU University of Amsterdam). The conference provided an excellent snapshot of state-of-the-art chromatography.

Meeting report

Emerging contaminants in waters and soils, practical considerations: sampling, analysis and consequences

James Lymer (ECG), Richard Allen (WSF), Kevin Pryor (WSF), Stephen Mudge (INEF)

This scientific meeting aimed to present a number of perspectives on the chemical sciences of emerging contaminants in soil and water environments. It was jointly organised by the RSC Environmental Chemistry Group (ECG), the RSC Water Science Forum (WSF) and the International Network of Environmental Forensics (INEF), and was held at The Source, Sheffield on 4th March 2015. Fifty-six delegates attended from a wide range of organisations including consultancies, regulators and academia.

Environmental contaminants may be broadly classified into two groups:

Common Environmental Contaminants are substances with known chemical and toxicology properties, such as trichloroethene, that are present in the environment due to historic lack of regulation, inadequate use and storage, and waste disposal. In the UK. their use pre-dated the Environmental Protection Act 1990, and they are now subject to remediation in soil and groundwater systems. These substances are now largely banned from use or are tightly regulated for use by operators, and in their treatment/disposal by waste companies through Environmental Permitting Regulations (as amended), and hence are less likely to enter the environment.

Contaminants of Emerging Concern are substances not previously considered or known to be significant in the


Intake of raw water at a water treatment plant. Credit: Chaiyapruk Chanwatthana/Shutterstock

environment and may have no regulatory standard. Examples include pharmaceuticals and personal care products. Due to improved monitoring techniques and increasingly sensitive analytical methods, more emerging contaminants are being detected in the environment, particularly in surface water and groundwater. Emerging contaminants can be broadly defined as any synthetic or naturally occurring chemical or microorganism that is not commonly monitored in the environment but has the potential to enter the environment and cause known or suspected adverse ecological and/or human health effects.

In the developed world, there has been a gradual decrease in the environmental concentrations of common environmental contaminants such as heavy metals, polychlorinated biphenyls (PCBs), dioxins, and polyaromatic hydrocarbons (PAHs). This improvement is largely due to stricter regulations with improved monitoring, cleaner industrial processes and waste disposal practices. There is a now a focus on contaminants of emerging concern.

Data reported to the European Commission show that 40% of surface water resources in the European Union have an unknown chemical status, with many member states not monitoring priority substances.

Many of these newly recognized contaminants are produced industrially yet are dispersed to the environment from domestic, commercial, and industrial use including pesticide distribution to land, wastewater treatment effluent discharges, landfill sites, and sewage sludge spreading to land.

Some emerging contaminants are recalcitrant to conventional sewage treatment or drinking water treatment. Many are small and/or very polar molecules, which are difficult to remove by granular activated carbon filtration methods. Key receptors to these contaminants are humans who consume drinking water sourced from contaminated water and aquatic ecology.

Rakesh Kanda (Brunel University, London) began the event with a presentation entitled *Emerging and priority pollutants – the need for ultra-low trace level monitoring*. He explained that water is under threat from our increasing use of chemicals and the rapid urbanisation of our cities. Rakesh's research interests cover a range of topics related to the development and application of analytical techniques for the detection of environmental contaminants and for assessing animal and human exposure to compounds in the environment. The Water Framework Directive (WFD) uses environmental quality standards (EQS) for priority substances and priority hazardous substances as the criteria for the assessment of good chemical status. Robust environmental monitoring is essential for assessing the chemical status of water bodies. Data reported to the European Commission show that 40% of surface water resources in the European Union have an unknown chemical status, with many member states not monitoring priority substances. Reasons for the lack of monitoring include the analytical difficulties in detecting and quantifying analytes near the limit of detection, and, in general, the financial costs of ultra-low analytical measurements.

Graham Mills (Portsmouth University) and **Anthony Gravell** (Natural Resources Wales) gave a presentation entitled *Comparison of active and passive sampling in relation to contaminants of emerging concern*. They discussed sampling practices undertaken at surface water bodies for the purposes of obtaining water samples for chemical analysis and understanding contaminant concentrations. Research interests include the use of gas chromatography and mass spectrometry techniques in biomedical and environmental analyses as well as development of novel sample preparation methods in analytical chemistry and the use of high-field NMR in environmental toxicology. Graham is also very interested in the development of passive sampling devices to monitor water quality and the fate of pharmaceutical residues in the aquatic environment.

The next presentation, by **Dr Maria Romero-Gonzalez** (University of Sheffield) and **Dr Peter Skipworth** (Environmental Monitoring Solutions Ltd), was entitled *Measuring continuous concentration of mass pollutants in the aquatic environment*. The speakers reported on their work using surface-sensitive spectroscopic techniques to elucidate chemical bonding and mechanisms at the solid-water interface, as well as potentiometric methods and wet chemistry studies to quantify thermodynamic and kinetic models of reactive processes in model systems. They discussed the development and intended application of a continuous water monitoring instrument called MultiMEMS, which can detect phosphates, nitrates and metaldehyde in water bodies.

Marianne Stuart (British Geological Survey, Wallingford) spoke about *Emerging contaminants in groundwater in urban environments*. Her research interests include emerging contaminants and the impacts of hydraulic fracturing. Marianne highlighted the increasing detection of micro-organic compounds in the groundwater environment as advances in analytical techniques are leading to lower detection limits. These compounds include pharmaceuticals and personal care products, lifestyle compounds (nicotine, caffeine) and food additives and their metabolites. Sources in the urban environment include sewage treatment effluent and landfill site leakage. Marianne reported on groundwater monitoring studies in the Sherwood Sandstone aquifer at a site in Doncaster and another in Nottingham, which indicated that emerging contaminants are present at significant depth (>50 m) and that wastewater was the likely source.

A presentation by **Barbara Kasprzyk-Hordern** (University of Bath), entitled *Stereochemistry of pharmacologically active compounds: a new paradigm in environmental analysis and risk assessment*, focussed on the significance of chiral organic contaminants such as pharmaceuticals in the environment. Chiral pharmacologically active compounds (PACs) enter the environment mainly through sewage, waste effluents from manufacturing processes, runoff and sludge. They are bioactive, ubiquitous and persistent, with synergistic properties. Considerations of the environmental fate and effects of these substances do not often take into consideration that the enantiomers of the same substance can have different effects. Barbara presented results from the monitoring of several wastewater treatment plants and receiving waters and considered the implications of enantiomer-dependant fate and ecotoxicity of PACs.

View of the lake at Schloss Steinhöfel, Brandenburg, Germany. *Many water resources in the EU have unknown chemical status. Credit: JFU*

Zulin Zhang (James Hutton Institute) spoke about *Short- and long-term temporal trend of organic contaminants in soils following single or multiple applications of sewage sludge to pastures*. Zulin is interested in investigating environmental chemical behaviour (source, transport and fate), effect and risk assessment of organic contaminants. He is also interested in developing new analytical and monitoring techniques/methods for emerging organic contaminants of different environmental matrices, with an emphasis on compounds that enter the food chain and have an effect on animal and human health.

Christine Switzer (University of Strathclyde) gave a talk on *Emerging contaminants in soils: challenges and opportunities from quantification to remediation*. Her research interests lie in the areas of contaminant fate, transport, and remediation. Christine is particularly interested in aggressive remediation technologies for contaminated soils and emerging contaminants in the environment such as fire retardants and other micro-pollutants. She discussed the practical issues concerned with detection and quantification, contaminant release, mass transfer, and finally remediation.

Simon Parsons (Scottish Water) concluded the symposium with his lecture on *Sustainable water treatment*. Simon received the RSC's Sustainable Water Award in 2014. His presentation centred on the priorities for improving drinking water. In particular, he talked about lead removal, reducing disinfection by-products, and removal of colour. He also considered the impact of the current public perception of chemicals in drinking water. He highlighted a number of internationally significant potable (drinking) water quality incidents which resulted from the removal of disinfectants from the treatment process. He drew attention to the usually high drinking water quality throughout the developed world and the methods different countries had used to achieve that.

Copies of the presentations from the speakers are available from the WSF and ECG websites (www.rsc.org/wsf and www.rsc.org/ecg).

Meeting report

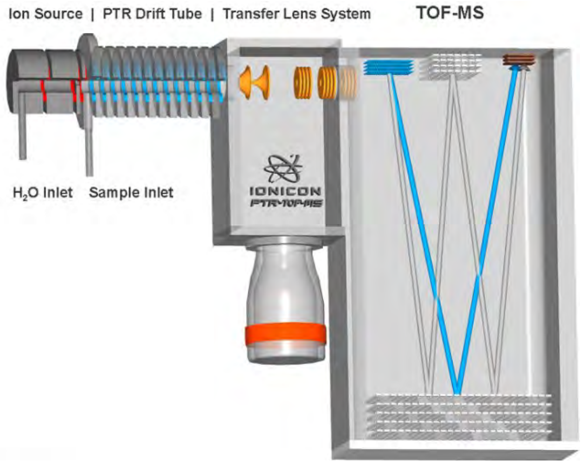
Soft ionisation mass spectrometric techniques and the environmental sciences

Emily House (Lancaster University; e.house1@lancaster.ac.uk)

On 10th December 2014, the Environmental Chemistry Group and the Molecular Physics Group of the Institute of Physics co-organised a half-day meeting to discuss recent applications and developments of soft chemical ionisation mass spectrometric techniques in the field of environmental sciences, with a focus on the areas of atmospheric chemistry and physics. This followed on from two successful meetings on the same topic in 2012 and 2013. The meeting comprised four talks from invited speakers; each forty minute presentation was followed by ten to fifteen minutes of questions and discussion.

The first talk, given by **Professor Thomas Karl** (University of Innsbruck, Austria), was entitled *Eddy Covariance Measurements of NMVOC using PTR-(Q)MS, PTR-TOF-MS and PTR-QI-TOF-MS.* The speaker began with an overview of the role of non-methane volatile organic compounds in determining tropospheric ozone levels, the oxidative capacity of the atmosphere, and the formation of organic aerosols. He highlighted the need for reducing uncertainties associated with NMVOC (non-methane volatile organic compounds).

Thomas Karl discussed the range of spatial and temporal resolutions covered by different approaches to the study of NMVOCs, from leaf level through to earth observation, and then focussed on tower-based and airborne flux measurements. These techniques can offer temporal resolutions of less than one minute; periods of measurement from some tower sites extend over several years. The techniques used to quantify (NMVOC) fluxes have advanced from more indirect gradient methods through virtual disjunctive eddy covariance (pioneered by Professor Karl) to direct eddy covariance of a large number of compounds with the recently developed PTR-ToF-MS (Proton transfer time-of-flight mass spectrometry) method.

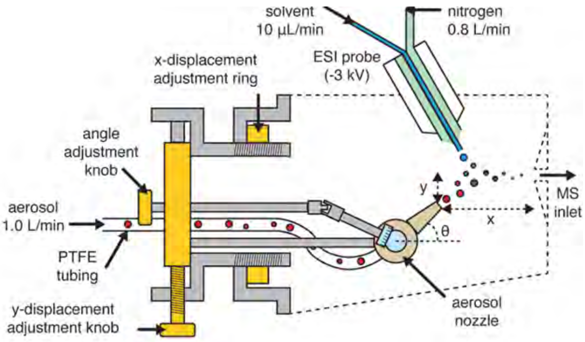


Schematic diagram of a proton transfer time-of-flight mass spectrometer (PTR-TOF-MS). *Credit: Thomas Karl, University of Innsbruck*

Thomas Karl stressed the particular importance of flux-based techniques in the tropics, where large species diversity hampers calculation of emissions by scaling up leaf-level measurements. Recent advances including the use of an Ionicon PTR-ToF-MS for measurement of methanol fluxes by eddy covariance, with the high mass resolution enabling methanol to be distinguished from isobaric ions. PTR-MS flux data across the USA and South America have been used to derive upper and lower bound estimates of dry deposition of the isoprene oxidation products methyl vinyl ketone and methacrolein to vegetation. Professor Karl also showed airborne measurements of anthropogenic VOCs in Mexico City and discussed source distributions. In the final part of the talk, he introduced a newly developed technique, proton transfer reaction quadrupole interface time of flight mass spectrometry, and its current application to measuring NMVOC fluxes, including benzene, over the city of Innsbruck. The speaker concluded with a summary of progress in CIMS (chemical ionisation mass spectrometry) over the last fifteen years and the consequent advances in flux quantification.

The second speaker, **Dr Racheal Beale** (Plymouth Marine Laboratory), described her work in quantifying concentrations and air-sea exchange of acetone *in situ*. She discussed the importance of acetone in the troposphere and the uncertainty in the extent and drivers of net oceanic exchange resulting from the sparse number and limited duration of measurements. The speaker described a novel membrane inlet PTR-MS technique for measuring acetone in seawater and demonstrated its application during several field campaigns. These included: ICON, where concentrations were measured from the Mauritanian upwelling during April and May 2009; the Atlantic Meridional Transect (AMT) 19 and AMT 22 research cruises, which travelled from the UK to Chile during October and November in 2009 and 2011 respectively; and long term (January 2011 to March 2012) weekly measurements at a research station 10 km off the Plymouth coast.

Seawater acetone concentrations measured during AMT 19 and 22 ranged from 2 to 24 nM and 5 to 36 nM respectively. Surface seawater concentrations during the cruises were comparable to the highest concentrations observed in the North Atlantic Gyre, where biological activity is low, and were highest in the high temperate latitudes. High concentrations were also observed in the eutrophic Mauritanian upwelling. During AMT 22, eddy covariance air-sea flux measurements were also undertaken using PTR-MS and compared with air–sea flux predicted from a two-layer model using the measured water and air concentrations. Observed and predicted acetone fluxes were in good agreement. During AMT 22, the Atlantic Ocean was a net sink for acetone at high northern latitudes and a net source in the subtropics, whereas the South Atlantic represented a zero net flux. Dr Beale concluded with planned future work, including the use of a switchable reagent ion source to aid separation of glyoxal and propanal contributions to the acetone signal.



Extractive electrospray ionization (EESI).
Credit: Markus Kalberer, University of Cambridge

In the third talk, **Dr Markus Kalberer** (University of Cambridge) gave a comprehensive overview of the use of soft ionisation ultra-high resolution mass spectrometry (UHRMS) for characterising the organic fraction of atmospheric particles. The average chemical composition of tropospheric aerosol includes a large fraction of organic material. The chemical composition of this material is important, for example in determining health impacts, but largely unknown due to challenges in determining temporal and spatial variability, measuring trace quantities, and characterising complex mixtures. Dr Kalberer explained how the high mass resolution and accuracy of UHRMS can help to meet these challenges because they enable us to determine elemental composition. Though less able to measure the entire chemical space (polarity, solubilities, functional groups), the reduced fragmentation produced by soft atmospheric pressure ionisation is useful for analysing complex mixtures in laboratory-based smog chamber experiments and also for characterising samples collected in the field. Dr Kalberer described the use of techniques such as Nano -Desorption Electrospray ionization (DESI), Liquid Extraction Surface Analysis (LESA) and Extractive Electrospray ionization (EESI) ("online ESI") to minimize sample workup and associated artefacts and to provide temporal information of increasing resolution.

In the final talk, **Dr Gavin Phillips** (University of Chester) described the use of iodide chemical ionization mass spectrometry (ICIMS) for the measurement of peroxyacetyl nitrate (PAN) and peroxyacetic acid (PAA) using alternatively heated and ambient temperature inlet lines. He contrasted measurements made at a boreal forest site in Finland (HUMPPA-COPEC campaign) with those from a mountaintop site in Germany (PARADE). PAA was found to be a large proportion of the sum of PAA and PAN during the HUMPPA campaign, which was characterised by above average temperatures, high BVOC (biogenic volatile organic compounds), and low NO_x mixing ratios. In contrast, during the PARADE campaign PAN dominated, reflecting lower temperatures and NO_x levels. Dr Phillips moved on to the use of ICIMS alongside aerosol mass spectrometry to investigate production of $ClNO_2$ through uptake of N_2O_5 on chloride containing aerosols in the field.

The meeting was attended by *ca.* 40 delegates, and it was agreed to hold a fourth meeting in the autumn of 2015 – details to follow.

Meeting report and abstracts

New developments in the analysis of complex environmental matrices

Over 80 delegates and speakers attended this one-day meeting held on Friday, 6th February 2015 at the Royal Society of Chemistry, Burlington House, London. The meeting was organised by the Environmental Chemistry Group (Dr Roger Reeve, Mr Ian Forber) and the Separation Science Group (Professor Graham Mills), and aimed to update delegates with recent developments in analytical instrumentation that make it possible to simultaneously analyse numerous pollutants in complex matrices using minimal sample clean-up. There was a focus on analysis of solids, liquids and gases by liquid or gas chromatographic separation (LC or GC) with mass spectrometric (MS) detection, but one nuclear magnetic resonance (NMR) metabolomics investigation was also presented. Laboratory and field analytical techniques were covered, along with the requirements for high sensitivity and specific analyte identification in complex matrices.

There were eight presentations by speakers from UK academic institutions, agencies and industries. A keynote lecture was given by **Professor Damià Barceló** (CSIC, Barcelona, Spain). Professor Barceló has an international reputation for the analysis of pollutants in water.

Professor Graham Mills (University of Portsmouth, UK) opened the meeting, welcoming the delegates and chairing the first five presentations during the morning session. Lunchtime gave opportunities to network and to inspect sponsors' displays. The afternoon session started with the keynote lecture delivered by Professor Barceló, and was chaired by **Dr Roger Reeve** (University of Sunderland, UK).

High resolution mass spectrometry provides novel insights into products of human metabolism of organophosphate and brominated flame retardants *Dr Mohamed Abdallah (University of Birmingham, Birmingham, UK)*

Indoor dust has been consistently identified as a major pathway for human exposure to flame retardants. Few studies have been made on metabolic pathways. Many of the studies investigate the banned polybrominated dibenzofurans (PDBEs), some with alternative retardants and only a few mimicking realistic *in vivo* situations. The current work studied the metabolism of mixtures of brominated and organophosphate flame retardants applied to human hepatocyte cultures as a dust sample and as a synthetic mixture containing similar concentrations of the retardants. The dosage of the cells was designed to be equivalent to 12 mg dust based on a 12.3 kg toddler ingesting 200 mg dust/day. After 24 hours incubation, the metabolites were extracted with methanol and analysed by ultra-high performance liquid chromatography-electrospray ionisation mass spectroscopy (UPLC-ESI-Orbitrap™ MS). Metabolite identification was by MS full scan: four

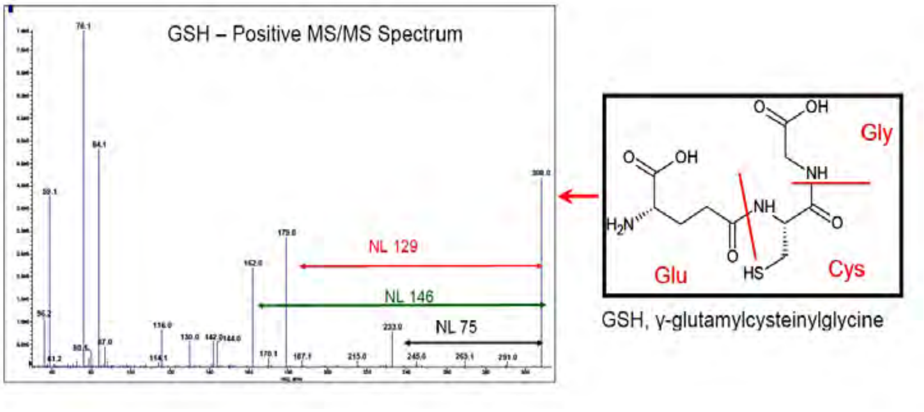


Figure 1. Confirmation of Phase II metabolites by a MS/MS method.

digit accurate mass with confirmation by MS/MS (**Figure 1**). Phase I and Phase II metabolism were identified, and all ion fragmentation spectra were useful for identification of the conjugates. Details of the metabolic pathways of each compound type were determined.

Use of metabolomics in solving environmental problems

Dr Jake Bundy (Imperial College, London, UK)

Is it possible to study environmental effects by metabolomic analysis of a single species under a variety of stressors such as pollutants, climatic conditions and feeding levels? Earthworms were studied in the laboratory and at 17 sites (including 6 polluted and 6 control sites) in the UK for which soil properties (TOC, pH, moisture, temperature), and levels of metallic contamination were determined. A total of 300 worms were studied. $^1H/^{13}C$ heteronuclear NMR experiments were undertaken on tissue extracts, restricting data acquired to the 'interesting' betaine region to reduce acquisition time (**Figure 2**). Although it proved possible to link some laboratory stresses to field effects, there was large inter- site and intra-site variation and the model was not predictive. The number of earthworm genotypes makes this difficult (two cryptic species are found in the UK and there are probably several more across Europe). Using this approach, metabolites were identified which could distinguish the different genotypes.

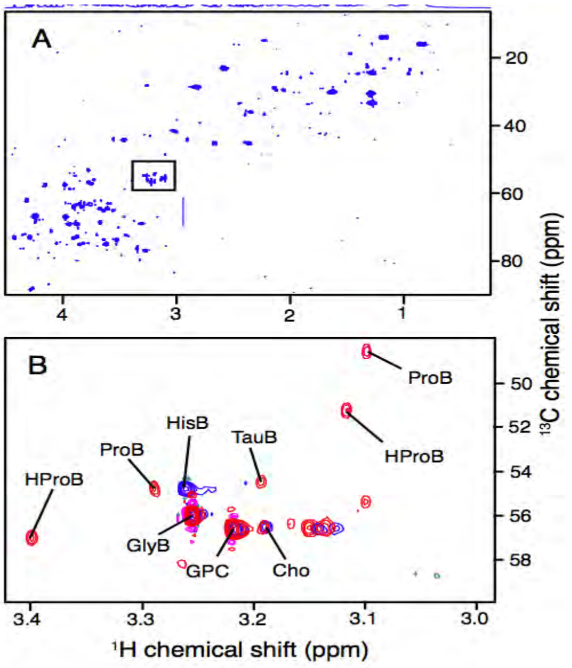


Figure 2. Restriction of $^1H/^{13}C$ NMR data to the betaine region to cut acquisition time.

Monitoring of polar pollutants in surface waters using Chemcatcher®-based passive sampling methods

Anthony Gravell (Natural Resources Wales, Llanelli Laboratory, Wales)

Passive sampling devices can be deployed directly in rivers for several weeks to give time-weighted average concentrations of pollutants. These avoid the 'hit and miss' nature of taking spot samples of water. The acid herbicides monitored were highly water soluble and almost completely ionised at environmental pH, so needed to be extracted by ion-exchange rather than conventional adsorption. Chemcatcher® passive samplers using Empore® anion-exchange discs were deployed in the laboratory and field (10-14 days sampling time) and compared to existing water monitoring methods. Measurements were taken during the linear uptake phase (before equilibrium), where the concentration of pollutant was proportional to the mass of the disc, the sampling rate and the exposure time. For field applications a polyethersulfone membrane was added to the Chemcatcher® to increase the time to reach equilibrium and to improve disc integrity. Typical field concentrations of herbicides were in the low ng/L range. Measurements below the detection limit of the spot sampling method were possible using this novel approach.

Analysis of marine biotoxins in shellfish

Dr Andrew Turner (CEFAS Weymouth Laboratory, Weymouth, UK)

Paralytic shellfish poisoning algal toxins have been reported to cause severe illness in humans at 5.6-2058 µg Saxitoxin (STX) equivalents/kg and have a maximum permitted level of 800 µg STX equivalents/kg in shellfish tissue. Testing until 2006 was by mouse bio-assay and is still the official reference method. An alternative, chromatographic, method is post-column oxidation liquid chromatography with fluorescence detection (LC-FLD). However, this technique needs two columns/systems to run each sample, has very short column lifetimes and is prone to matrix effects giving false positive and negative results. Another approach uses hydrophobic interaction chromatography MS/MS (HILIC-MS/MS), but has sensitivity problems, long run-times, matrix interference, and ion-source fragmentation implications. Current work at CEFAS is investigating these analytical problems. Comparison of Xevo TQ® to Waters Acquity® showed a 10-50 times increase in sensitivity of the Xevo TQ®, which enabled very low limits of detection/quantification for standards. Fast UPLC was ideal for fast cycle time. Fragmentation mitigation included using negative mode rather than positive ionisation for some transitions, and optimisation of the HILIC separation. Matrix effects could not be removed by simple dilution techniques. Carbon solid-phase extraction removed 90-100% Na, Mg, K and Ca, although some Na formate remained. With these improvements the method was fully validated for 12 species of interest and showed good equivalence with the LC-FLD methods.

Pollution by polyisobutenes: a sticky problem for seabirds *Professor Steve Rowland (University of Plymouth, Plymouth, UK)*

Polyisobutenes (PIBs) are a generic group of oligomeric to polymeric, liquid to solid hydrocarbons, which are used in numerous industrial applications, including viscosity modifiers, lubricating oil additives, cosmetics (e.g. as lip glosses) and in chewing gum. PIBs have been manufactured since the 1930s, but currently they are made by well-controlled reactions, which produce alkenes and a larger proportion of oligomers with terminal double bonds. Some of these so-called 'highly reactive' (HR) PIBs, are then converted to other derivatives for use as ashless detergent additives for lubricants. These multiple uses require global movement of PIBs by road, rail and ship; some HR-PIB manufacturers are based in Europe, USA and Korea. Several marine pollution events involving PIBs or PIB derivatives have occurred, presumably from shipping discharges. Indeed the extant classification of PIBs in 2013 allowed for small legal discharges from ships at sea. In January and April 2013, discharges of what was identified by chemical analysis in Plymouth University laboratories as HR-PIB and confirmed by a laboratory in Germany, apparently polluted seabirds in the English Channel. Thousands of birds died and a media storm resulted. The background, analytical data, possible origins and a discussion of the possible fate of the HR-PIB spills were presented. Techniques used included NMR, infrared (IR) and high temperature GC-MS. The findings helped wildlife agencies (e.g. RSPCA, RSPB) to achieve a change in the classification of PIBs.

LC tandem MS strategies for the analysis of contaminants of emerging concern in water, soil and sediment samples *Professor Damià Barceló (CSIC, Barcelona, Spain)*

Endocrine disrupting compounds (EDCs) include a wide range of chemicals that are thought to disrupt the endocrine function of fish and mammals. Total EDC concentrations are found in the ng/L to µg/L range in river water samples and in the ng/g range in sediments. Concentrations were determined by a dual column LC switching system in which 2-5 mL sample were loaded onto a pre-concentration column, then eluted onto the analytical column with MS/MS analysis. On-line turbulent flow chromatography was used to investigate degradation products of tetracyclines after enzymatic degradation of contaminated waters. This was coupled to an LC-(ESI)-LTQ Orbitrap™ liquid chromatography-mass spectrometry system. Turbo flow uses large particle columns (30 µm or greater) and eliminates large molecules (e.g. peptides and proteins), and retains smaller molecules on the column. Separation is achieved by the difference in diffusion rates according to compound size. MS was achieved by full scan ESI, positive and negative ionisation, and ion trap with MS2 fragmentation of the five most intense peaks from the full scan. Iodinated X-ray contrast media compounds are frequently detected in wastewaters at µg/L concentrations and in surface waters up to 0.1 µg/L. The small number of commercially available standard compounds can readily be photolysed to produce over 100 transformation products. These were studied in laboratory samples, after simulated environmental degradation, and then in surface water samples. Once

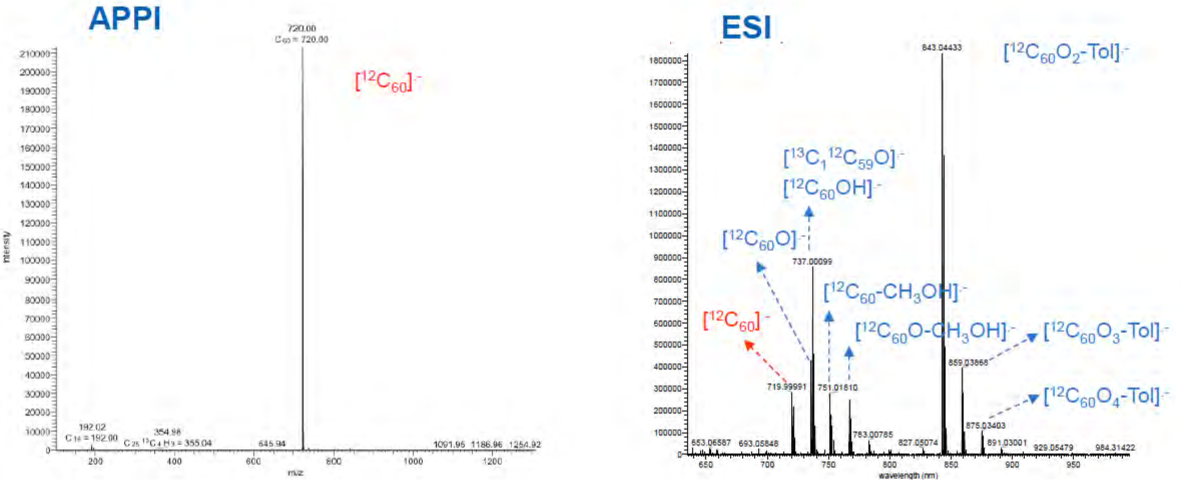
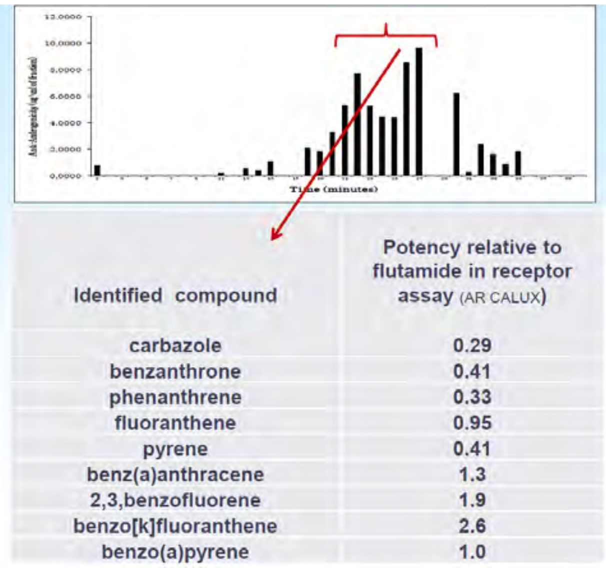


Figure 3. Comparison of atmospheric pressure photoionisation (APPI) and electrospray ionization (ESI) for fullerene analysis.

detected and prioritised, a number were isolated by semi-prep LC and their structures confirmed by ^{13}C and ^{1}H NMR spectroscopy. Initial screening was by high resolution MS, but once confirmed and a standard isolated, low resolution MS could be used. Fullerenes are emerging new pollutants and can have non-anthropogenic origins, such as volcanoes and forest fires, as well as industrial combustion-related sources. After extraction and chromatographic separation, fullerenes were analysed using atmospheric pressure photo-ionization MS (MS-APPI). This technique was found to be approximately 100 times more sensitive than MS-ESI (**Figure 3**). Fullerenes were extracted from water and sediments by liquid-liquid extraction and ultrasonic extraction, respectively. A pyrenylpropyl-bonded silica chromatographic column (buckyprep column) was used, with toluene as the mobile phase. Concentrations of C60 and C70 were found in the high pg-µg/L range in wastewater effluents, and concentrations were approximately a factor of 10 lower in river water close to the effluents. There was no clear relationship between the river water and discharge concentrations, which would suggest other inputs (e.g. atmospheric deposition). C60 and C70 were detected in 91% of urban soils samples studied in low pg/g concentrations.

Aspects of drinking water quality: the analysis of disinfection by-products *Gavin Mills (Severn Trent Water Ltd., UK)*

Analysis of halogenated and other compounds produced by disinfection is required in order to comply with drinking water supply quality standards. Trihalomethanes (THMs) have a PCV (prescribed concentration or value) of 1000 µg/L. De-chlorinated water samples are analysed by headspace GC-MS, with sodium chloride added as a matrix modifier. On-line monitoring can reduce costs by minimisation of additional treatment processes. Bromate, produced by ozone treatment of raw water containing bromide (PCV = 10 µg/L) can be analysed by ion-exchange chromatography detected by post-column derivatisation and UV, bromide, ClO_2^- and ClO_3^- detectable by conductivity. *N*-Nitrosodimethylamine is produced by ozonolysis of water containing specific pesticides (Action Levels 1, 10, 200 ng/L). Analysis is prone to interference if simple GC-MS is used. Confirmation can be made by GC-triple quadrupole MS (GC-QQQ). Analysis of halophenols by GC-QQQ allows reduced sample volumes. and automated sample preparation with the use of an Instrument Top Sample Prep cartridge.



Identified compound	Potency relative to flutamide in receptor assay (AR CALUX)
carbazole	0.29
benzanthrone	0.41
phenanthrene	0.33
fluoranthene	0.95
pyrene	0.41
benz(a)anthracene	1.3
2,3,benzofluorene	1.9
benzo[k]fluoranthene	2.6
benzo(a)pyrene	1.0

***Figure 4**. Examples of bioavailable anti-androgens present in clam tissues and sediment extracts.*

Screening for novel anti-androgenic contaminants in environmental samples using mass spectrometry combined with bio-assay procedures

Professor Elizabeth Hill (University of Sussex, Sussex, UK)

Although the concentrations of anti-androgenic compounds present in environmental samples are too low to have a direct effect on fish, they have previously been shown to contribute to feminisation of fish when in combined with estrogens. Professor Hill described a screening process for detecting anti-androgenic compounds using GC-MS and liquid chromatography/time-of-flight MS (LC-TOFMS) combined with a bio-assay. Samples downstream of sewage effluent were extracted by silicone strips or low-density polyethylene flat tubing for compounds with log $K_{OW} > 4$. For compounds with log $K_{OW} < 4$, Polar Organic Chemical Integrative Samplers with Oasis HLB sorbent were used for pharmaceuticals and ENV+/Ambersorb/Biobeads for pesticides. The extracts were fractionated by reversed-phase HPLC, and fractions tested for anti-androgenic activity. Further studies identified anti-androgens in clams exposed to waste-water effluent and widespread anti-androgenic activity in coastal sediments around the English Channel (**Figure 4**). Bio-assay-directed analyses can be a critical tool to identify causative agents for toxicity.

New developments in GC/MS and GC/PID instrumentation for rapid on-site analysis of trace environmental contaminants *Dr Andrew Hobson (Quantitech Ltd, Milton Keynes, UK)*

Commercial GC-photoionisation and GC-toroidal ion trap instruments have a range of environmental applications in the field. The GC-toroidal ion trap instrument (**Figure 5**) incorporates a capillary column, heating wire and temperature sensor wrapped together. Typically, samples are introduced after pre-concentration by solid-phase microextraction. Examples of use include

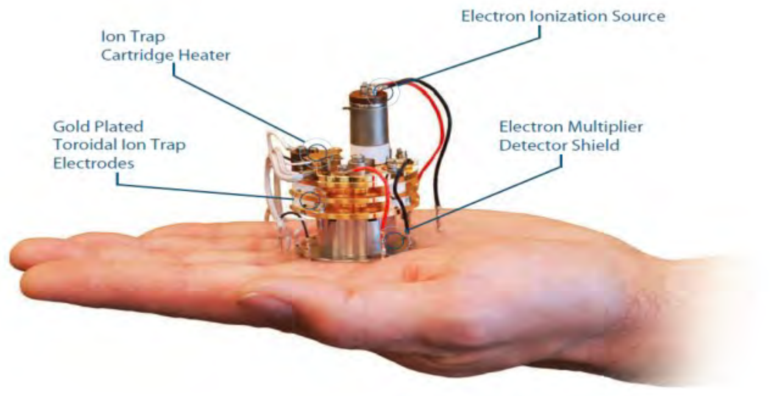


***Figure 5**. Ion trap module in the GC-toroidal ion field trap instrument.*

halomethanes in water over the range 10-100 ppb and geosmin (octahydro-4,8*a*-dimethyl-4*a*(2*H*)-naphthalenol) (responsible for odour in rain and earthy taste in fish) at 1ppt in water. The GC photoionisation instrument incorporates a pre-concentration stage where compounds sparged from a sample are absorbed on an application-specific sol gel. Heating releases the concentrate onto the 2.5 m, 0.8 µm OV-1 GC column. A typical application would be the analysis of ten volatile organic compounds in six minutes using a 40-100 °C temperature gradient. The portable nature of the instruments means that they can be left *in situ* for long-term analysis of contaminants. **Figure 6** shows the influence of metrological conditions on tetrachloroethylene intrusion into an indoor environment from contaminated sub-soil.

The meeting closed with general agreement of a thoroughly worthwhile day introducing many new methods for complex matrices using minimal sample clean-up. A similar meeting is likely to be held in early 2017.

These abstracts were prepared by **Roger Reeve**, **Graham Mills** and **Ian Forber** based on the presentations and slides supplied by the speakers. The industry meeting sponsors were Agilent Technologies, Crawford Scientific, LGC, Markes International, SCIEX, Shimadzu, Sigma-Aldrich, Thames Restek, Thermo Scientific and Waters. Financial support is also acknowledged from ESED.

Presentation slides are available from www.rsc.org/Membership/Networking/InterestGroups/Environmental/PastEvents

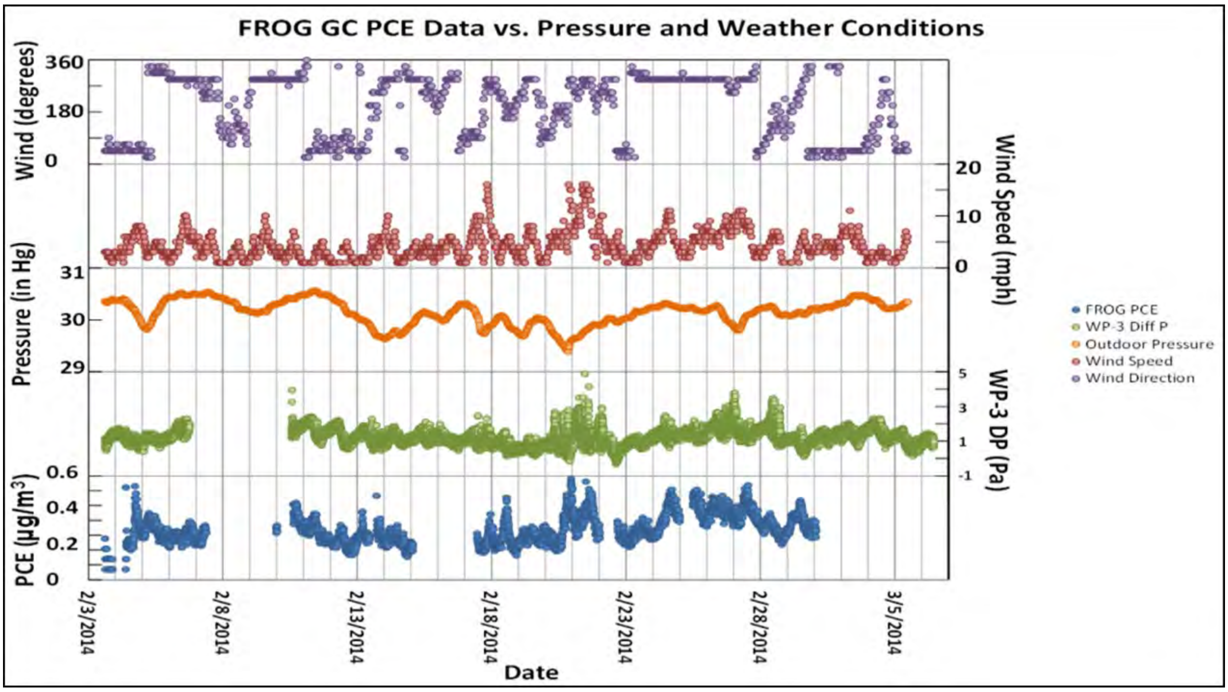


***Figure 6**. Changes in tetrachloroethylene concentrations in an indoor environment from contaminated sub-soil related to metrological conditions.*

Book Review

Geoengineering of the Climate System

Reviewed by Zoë Fleming (University of Leicester)

Published by the Royal Society of Chemistry in 2014 as volume 38 of the series Issues in Environmental Science and Technology, *Geoengineering of the Climate System*, edited by R. E. Hester and R. M. Harrison, gives a thorough overview of current advances and possibilities in geoengineering.

Making brighter clouds. *One proposed geoengineering method aims to create brighter clouds through injecting salt. The image shows a sunset behind clouds and aircraft contrails. Credit: Wollertz/Shutterstock*

With an average CO_2 rise of about 2 ppm per year and an atmospheric CO_2 concentration of close to 400 ppm in January 2015, it is imperative that we look into ways of decreasing atmospheric CO_2. The strong message from this book is that there is no miracle cure: only through a multi-faceted solution can we try to stabilise the Earth's climate. Governance and political and moral issues are brought into the technical discussions in a very convincing manner, and the economic issues of carbon taxing and creating market pressures for technology development and competition are clearly explained, helping to make geoengineering a modern and accessible topic for society and governments to consider.

The most up-to-date advances in the field are presented by fourteen authors in nine chapters that can be read as separate papers or as a well-rounded read from cover to cover. The introduction explains how human activity is changing climate, defines geoengineering, and introduces the arguments for and against it, as well as governance and political questions. The following chapters discuss carbon storage, carbon dioxide removal (CDR) with plants or algae, artificial trees, crops (biochar and albedo), brighter clouds, introducing stratospheric aerosol, and space-based solutions (artificial dust and reflecting discs). The final chapter explores the governance of solar radiation technologies.

Some chapters are more technical than others, with several diagrams of the nozzles and ultrasonic excitation mechanisms for injecting cloud condensation nuclei into the atmosphere and orbital diagrams explaining the space-based placement of dust clouds and reflecting discs. The scale of carbon sinks and energy expenditure becomes overwhelming but many of these numbers and other quantitative comparisons are contained in a host of tables throughout the book for quick referencing. Facts and anecdotes throughout the book fire up the imagination, such as the comparison between the weight of the Great pyramid of Giza and the disc that could offset the world annual CO_2 emissions.

A real flavour for a future world is built up throughout the narrative, shaped either through natural means (such as changing crops, use of biochar, and afforestration), efficiency and technology improvements or through science-fiction-like landscapes (fleets of trimarans on the oceans spraying clouds, millions of sea containers acting as artificial trees around the globe, and 10^8 ton reflective discs in space).

There is a recurring theme of how climate regulations could set global costs of CO_2 and thus incentivise developing technologies and remove the competitive advantage of fossil fuels relative to renewables and nuclear. All examples come from the UK or US, and it is sometimes hard to see how the governance and decision making could be undertaken on a global scale. Personal experience of one author in a large-scale geoengineering panel and the political and stakeholder issues in making the decisions illustrates how the proposals are assessed.

The last chapter gives the allegory of King Cnut, who had his chair carried to the sea shore, where he commanded the tide to halt. When it did not, he realised that no human, however important, can dominate and control the Earth. Can we go some way to right the harm we have done to it? Any efforts made to control the rising CO_2 levels must be governed wisely. Intergenerational justice, governance, and moral responsibility are intertwined in the text to make any reader think beyond the facts and figures.

Article

Non-targeted methods for identifying new and emerging persistent organic pollutants of environmental concern

David Megson (Ryerson University and Ontario Ministry of the Environment and Climate Change, Canada; david.megson@ontario.ca), Miren Pena-Abaurrea (Ryerson University and Ontario Ministry of the Environment and Climate Change, Canada) and Xavier Ortiz (University of Toronto and Ontario Ministry of the Environment and Climate Change, Canada)

The search for new and emerging persistent organic pollutants (POPs) has become an area of increased research in recent years. Analytical developments have made it possible to identify ever smaller concentrations of substances in environmental samples. Techniques are now so sensitive that polychlorinated biphenyl (PCB) concentrations can be monitored in a single blood spot (1). This article highlights the advantages of state-of-the-art techniques for non-targeted detection of potential new POPs.

Samples once deemed "clean" turn out to contain thousands of different chemicals. In some cases, these chemicals are not new to science; rather, developments in toxicology identify new hazards at a subcellular or chronic level, making these chemicals of emerging concern. Probably the best-known example is dichlorodiphenyltrichloroethane (DDT), which was used extensively as a pesticide for several decades until Rachael Carson alerted the world to the potential risks. Fifty years later, discussion continues over the use of this chemical. Although banned in most countries, DDT is still used in some developing countries to fight malaria because it is such an effective pesticide; yet exposure can result in severe human health impacts and damage to the environment (2).

Similar discussions are also underway over a new group of POPs: halogenated flame retardants. Various flame retardants have been used throughout human history, but flame retardants developed during the last century are manufactured on a scale large enough to pose a significant risk to the environment. Recent toxicological and analytical developments have identified the use of some of these organic flame retardants as a potential environmental concern. There is a debate as to whether the safety benefits from halogenated flame retardants outweigh the environmental risks as they are persistent, toxic and accumulate in humans and wildlife (3). PCBs were first manufactured and applied as flame retardants during the late 1920s. From the 1960s onward, several other chlorinated compounds, such as tris(2,3-dichloropropyl) phosphate (TDCPP) and tris(1,3-dichloroisopropyl) phosphate (TDCIPP) were used, followed by an increasing number of brominated flame retardants (BFRs), such as polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs). Following EU legislative measures and the inclusion of BDE formulations among the Stockholm Convention POPs, production and use of these substances have been phased out as they are replaced with supposedly safer

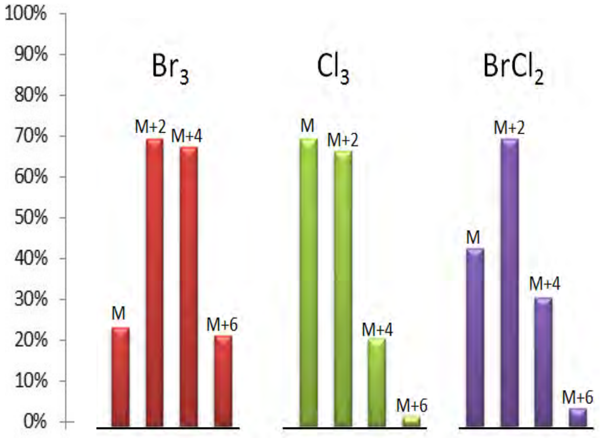


Figure 1. *Isotopic contribution of bromine and chlorine in compounds containing three halogens.*

alternatives. However, many of these replacements are chemically very similar to the substances they replace and are now being identified in environmental samples.

Many traditional analytical methods to measure POPs involve targeted analysis that only identifies specific compounds. Thousands of other chemicals in the sample go unmeasured. Non-targeted analysis allows screening for the presence of many different potential pollutants at the same time. This can lead to better risk assessment and more informed decision making, which can drive more effective legislation. The following two sections present complementary analytical techniques that highlight the benefits of non-targeted chemical analysis in the search for new and emerging POPs of environmental concern.

Multidimensional chromatography

Multidimensional gas chromatography, such as comprehensive two-dimensional gas chromatography (GC×GC), combines two gas chromatography columns of different phases using a modulator. This modulator traps compounds from the first column and reinjects them in a very tight band onto the second column, where further separation occurs. Enhanced separation is achieved because compounds are subjected to two independent separations that can significantly increase selectivity and sensitivity while reducing analysis times by eliminating injections on multiple chromatographic phases (4). After separation, halogen-selective detection techniques such as electron capture detection (ECD or micro-ECD) can be used for targeted analysis of POPs. However, a more selective and complete detection method such as time-of-flight mass spectrometry (TOFMS) is preferable for the identification of new compounds.

The advantage of mass spectrometry is that it provides more diagnostic information for each peak; chlorinated and brominated compounds can comparatively easily be recognized by their characteristic isotope patterns because of the high natural abundance of the $^{35}Cl/^{37}Cl$ and $^{79}Br/^{81}Br$ isotopes. With GC×GC-TOF MS, thousands of individual compounds can be simultaneously detected in a single environmental analysis. However, sample processing can become an extremely tedious task. By narrowing down the detection strategies for the early identification of halogenated compounds, both data interpretation and processing times can be greatly minimised. One valuable technique for the classification of specific compound classes is the use of pre-defined mass spectral scripting filters to look for the characteristic chlorine and bromine isotope patterns (**Figure 1**).

An example of the successful use of GC×GC and mass spectral scripting tools was the identification of a novel mixed halogenated carbazole in rural sediments of Ontario, Canada (5). The MS script developed by Pena-Abaurrea *et al.* was able to recognise a generic isotope pattern that enabled the simultaneous detection of chlorinated, brominated, and mixed halogen-substituted compounds in a single classification. Among the

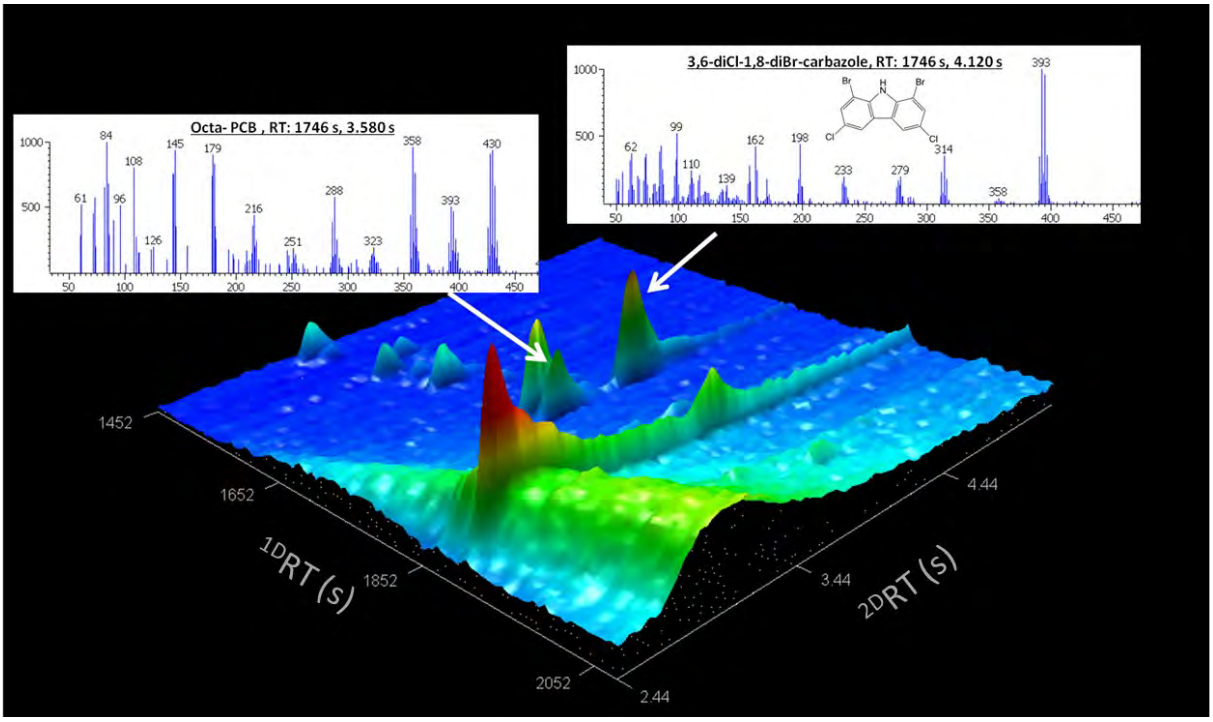


Figure 2. *This two-dimensional chromatogram from an Ontario sediment sample shows the separation of 1,8-dibromo-3,6-dichlorocarbazole from an octa-PCB with the same ^{1D}RT and same isotope cluster (5).*

hundreds of thousands of potential chemicals identified in the sample, the script function identified a particularly prevalent and apparently novel contaminant. The mass spectral fragmentation pattern showed losses of chlorines and bromines, and the odd molecular weight suggested the presence of at least one nitrogen atom in the molecular structure. Additional experiments using high-resolution MS techniques, aided by synthesis of suspected standard solutions of the proposed molecular structure, confirmed the identity of the unknown chemical as 1,8-dibromo-3,6-dichlorocarbazole. This previously unknown carbazole eluted at the same first dimension RT (1DRT) as an octa-PCB, and had a molecular ion cluster at m/z 393 that matched with a fragment observed in the mass spectrum of the octa-PCB (**Figure 2**). It may therefore have been masked in previous one-dimensional analysis by the octa-PCB, as the chromatography and low-resolution mass spectrometer would have been unable to distinguish the two compounds. Based on the structural similarity of the new chemical with well-known POPs, in particular dibenzofurans, the authors carried out toxicological tests. The toxicity of the carbazole was comparable to that of the hepta- and octa-chlorinated dibenzofurans and non-ortho PCBs. The carbazole was recorded in the sediment in concentrations similar to or higher than the sum of marker PCBs, making it environmentally relevant (5).

The source of this new contaminant is not clearly understood. Only two papers have proposed hypotheses about the release of carbazoles to the environment; each points to a different anthropogenic and natural origin (6, 7). The identification of this novel compound would not have been possible with standard single dimensional chromatography and low-resolution MS, highlighting the effectiveness of multidimensional chromatography and high-resolution MS to identify new and emerging persistent organic pollutants of environmental concern.

Ultrahigh resolution MS

After a chromatographic separation of analytes in a sample, detection is usually carried out by conventional high-resolution (with a resolution of 10,000), time-of-flight or tandem MS. These approaches are widely used to analyse legacy pollutants such as PCBs, polychlorinated dibenzo-p-dioxins, furans and pesticides. Unfortunately, these targeted methods do not take into account the presence of other unknown compounds with a potentially negative environmental impact. In the cases of dioxins, PCBs, and other related aromatic POPs, the corresponding mass spectra are very alike, and because these chemicals are so similar they often have similar retention times on a GC column. If chromatographic techniques cannot separate these compounds and low-resolution mass spectrometry is used, it will not be possible to distinguish the different ions; many compounds will go undetected and may be falsely recorded as one compound. Therefore, in the search for new and emerging contaminants of concern it is important to have a high mass accuracy to be able to distinguish different compounds of a similar mass.

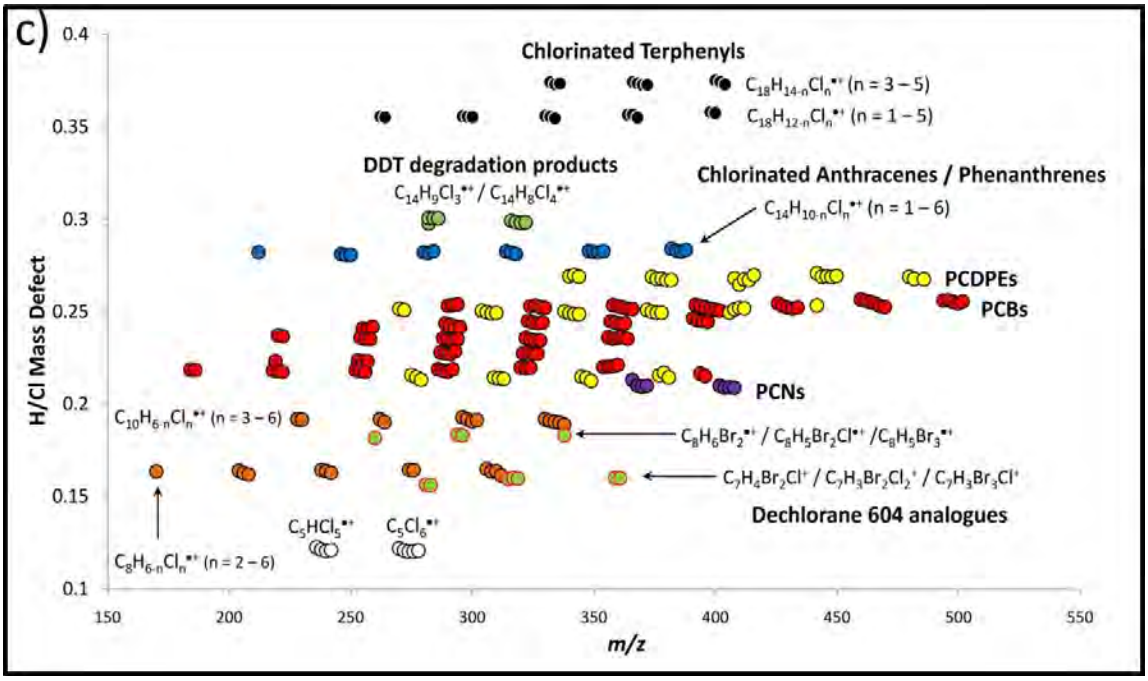


Figure 3. *Expanded view of the mass defect plots using the H/Cl and mass scale obtained from a sample of an extract of Lake Ontario lake trout. Reproduced with permission from reference* 10. *Copyright Springer-Verlag, Berlin, Heidelberg, 2013.*

Instruments such as the Orbitrap mass spectrometer or Fourier transform ion cyclotron resonance mass spectrometer (FTICRMS) can differentiate nominally isobaric ions with very similar exact masses. These ultrahigh resolution techniques (with a resolution >500,000) provide an excellent mass accuracy, which can be used to assign elemental compositions of the detected ions based on their exact mass. To date, FTICRMS is still the gold standard in terms of mass resolution and mass accuracy, making it a very powerful tool for the study of unknown compounds. The FTICRMS consists of a superconducting magnet refrigerated by liquid helium, offering magnetic fields between 3 and 12 Tesla. After an optional liquid or gas chromatographic step, analytes are ionized and accumulated in a hexapole for 0.5 to 2 seconds and sent to the magnet in packages. The ions are then excited by a radiofrequency, forcing them to spin in phase with a period that depends on the mass of each ion. When these ions get closer to the detector plates while spinning, a current is generated in a given frequency. The sum of all frequencies combined is finally deconvoluted applying the Fourier transform, and individual frequencies corresponding to each ion are converted to exact masses (8).

Due to the ultrahigh resolution of FTICR, the resulting mass spectra can be extremely complex, containing several thousands of peaks. One way to facilitate the visualization of these results and search for new persistent organic pollutants is to use mass defect plots. In these plots, each exact mass is plotted against its mass defect (exact mass minus nominal mass). Moreover, mass (which is expressed in the carbon scale, with an exact mass for carbon of 12.0000) can be converted to different mass scales to isolate and align series of structurally related compounds in the plot. Two of the most common mass scales for mass defect plots are the Kendrick mass scale (where CH_2 has an exact mass of 14.0000, thus aligning series of hydrocarbons) and the H/Cl scale proposed by Taguchi *et al.* (9) (where the exact mass of the exchange of a hydrogen by a chlorine atom is 34.0000, thus aligning families of halogenated compounds such as PCBs or dioxins).

An example of the successful use of ultrahigh resolution MS with mass defect plots was the discovery of several previously undiscovered contaminants, including chlorinated polycyclic aromatic hydrocarbons and mixed halogenated analogues of the flame retardant Dechlorane 604, in Lake Ontario Trout (**Figure 3**) (10). Traditional chlorinated compounds such as PCBs, DDT and dioxins are recognised contaminants in great lakes fish and as such are routinely monitored. The discovery of Dechlorane 604 trout was surprising, as this compound has a low potential for bioaccumulation. This finding has opened the question as to how the Dechlorane 604 analogues were produced, maybe through degradation in the environment or through a metabolic process in the fish. It also creates the need to establish if these newly identified contaminants are widespread, toxic and bioaccumulative which would make them contaminants of emerging environmental concern.

Conclusions

There are hundreds of thousands of potential chemicals of environmental concern and this list is continuously changing. Furthermore, these chemicals are released in a dynamic natural environment, where biogeochemical processes such as biodegradation, metabolism and photolysis can change these chemicals and produce new ones. It is thus a substantial challenge to identify which are the pollutants of concern. The two non-targeted analytical techniques presented here have proven to be highly effective in the search for new and emerging persistent organic pollutants of environmental concern.

Acknowledgements

The authors thank Karl Jobst (Ontario Ministry of the Environment and Climate Change) and Sean Comber (Plymouth University) for their constructive comments on this article. Miren Pena thanks Conservation Ontario for financial support with the Southern Ontario Stream Sediment Project (SOSSP) project.

References

1. D. G. Patterson, S. M. Welch, W. E. Turner, A. Sjodin, J. F. Focant, *J. Chromatogr. A* **1218**, 3274-3281 (2011).
2. M. Cone, 'Should DDT Be Used to Combat Malaria?', *Sci. Amer.* 2009, available at www.scientificamerican.com/article/ddt-use-to-combat-malaria/.
3. S. D. Shaw *et al.*, *Rev. Environ. Health* **25**, 261-305 (2010).
4. E. J. Reiner, K. L. Jobst, D. Megson, F. L. Dorman, J. F. Focant, Chapter 3, Environmental Forensics Analytical Methodology of POPs, in *Environmental Forensics for Persistent Organic*, G. O'Sullivan and C. D. Sandau, Eds. (Elsevier, 2013).
5. M. Pena-Abaurrea *et al.*, *Environ. Sci. Technol.* **48**, 9591-9599 (2014).
6. J. Mumbo, D. Lenoir, B. Henkelmann, K. W. Schramm, *Environ. Sci. Pollut. Res.* **20**, 8996-9005 (2013).
7. R. Parette *et al.*, *Chemosphere* **127**, 18-26 (2015).
8. A. G. Marshall, C. L. Hendrickson, G. S. Jackson, *Mass Spectrom. Rev.* **17**, 1-35 (1998).
9. V. Y. Taguchi, R. J. Nieckarz, R. E. Clement, S. Krolik, *J. Am. Soc. Mass Spectrom.* **21**, 1918-1921 (2010).
10. K. J. Jobst *et al.*, *Anal. Bioanal. Chem.* **405**, 3289-3297 (2013).

ECG Environmental Briefs **(ECGEB No 9)**

The atmospheric chemistry of HO_2 and organic peroxy radicals

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The lower part of the Earth's atmosphere (the troposphere, up to about 9 to 18 km) serves as a sunlight-driven reactor that removes emitted species from the atmosphere, but that can generate potentially harmful by-products such as ozone and particulate matter. This *ECG Environmental Brief* outlines the key chemical processes involved in this reactor system, with a focus on the role played by peroxy radicals.

ECG Environmental Brief No 3 (1) provided a nice introduction to the daytime chemistry of the troposphere. There, it was shown that sunlight-driven photolysis of ozone (O_3) in the presence of water vapour is a significant source of reactive hydroxyl radicals (OH) to the atmosphere:

$O_3 + h\nu\ (\nu < 340\ \mathrm{nm}) \rightarrow O(^1D) + O_2$ [R1]
$O(^1D) + H_2O \rightarrow OH + OH$ [R2]

These OH radicals are responsible for initiating the atmospheric removal of most trace gases, such as volatile organic compounds (VOCs), such as CO and methane:

$OH + CO \rightarrow H + CO_2$ [R3]
$H + O_2 + M \rightarrow HO_2 + M$ [R4]
$OH + CH_4 \rightarrow CH_3 + H_2O$ [R5]
$CH_3 + O_2 + M \rightarrow CH_3O_2 + M$ [R6]

In both cases, the product is a peroxy radical, HO_2 (H-O-O•) in CO oxidation and CH_3O_2 (CH_3-O-O•) in the methane case. These radical species are short-lived and highly reactive, particularly with NO:

$HO_2 + NO \rightarrow OH + NO_2$ [R7]
$CH_3O_2 + NO \rightarrow CH_3O + NO_2$ [R8]

Peroxy radical lifetimes are controlled by their proximity to NO emission sources, ranging from milliseconds in urban locations to minutes in pristine forests.

Consider now the combined effect of reactions [R3], [R4] and [R7]. We see that radical cycling is occurring, in which OH, H, and HO_2 are consumed and regenerated. The net effect is the oxidation of CO to CO_2 and NO to NO_2. Coupled with the facile daytime photolysis of NO_2,

$NO_2 + h\nu\ (\nu < 420\ \mathrm{nm}) \rightarrow NO + O$ [R9]
$O + O_2 + M \rightarrow O_3 + M$ [R10]

we see that NO and NO_2 also cycle between each other, generating ozone in the process. This reaction of a peroxy species with NO is the only method for generating tropospheric ozone, which is harmful to human and vegetative health and is an important greenhouse gas.

The cycling of radicals from OH, to H, to HO_2 and back to OH leads us to the concept of a radical family, in this case the HO_x family. Members of the family interconvert among each other rapidly, generally on a shorter time scale than family members are lost or produced. NO/NO_2 also interconvert rapidly and are referred to as NO_x. A similar story emerges when considering the net effect of [R5] through [R11]. Here, the CH_3, CH_3O_2, and CH_3O radicals cycle, along with OH and HO_2. Again, NO_x is cycled, ozone is generated, and methane is partially oxidized to formaldehyde, CH_2O:

$CH_3O + O_2 \rightarrow CH_2O + HO_2$ [R11]

The lifetime of the peroxy radical species exceeds that of the other species in the family, and their ambient concentrations are thus larger; typical daytime peroxy radical concentrations are 10^8 to 10^9 molecule cm^{-3}, whereas OH levels are commonly $\approx 10^6$ molecule cm^{-3}.

Peroxy radical chemistry

So far, we have considered only the simplest peroxy radicals, HO_2 and CH_3O_2. However, there can be thousands of different VOCs in the atmosphere, ranging in complexity from methane to monoterpenes (biogenic molecules with the formula $C_{10}H_{16}$) to diesel fuel components. There is a concomitant complexity in the range of peroxy radicals that can be generated. Thankfully, many reactions involving peroxy species are similar across the whole range of species. For example, all known reactions of peroxy radicals with NO have rate coefficients that vary over a fairly narrow range, ≈ (7-21) x 10^{-12} cm^3 $molecule^{-1}$ s^{-1} (2). Thus, knowledge of the detailed identities of organic peroxy radicals present is often less important than knowing the total peroxy radical concentration, and it becomes convenient to label the entire collection of atmospheric organic peroxy radicals as RO_2 (where R represents any organic fragment). The family of radicals that include R, RO_2, RO, OH and HO_2 are referred to by the general term RO_x (where R also encompasses hydrogen).

As seen above, the reactions of HO_2/RO_2 with NO are part of a radical cycling mechanism that consumes primary pollutants (VOCs) and generates ozone. Were this the only chemistry to happen, radicals would propagate forever. However, other reactions do occur, some that propagate radicals and continue ozone production chemistry, others that terminate HO_x and/or NO_x cycles. For example, the reaction of RO_2 with NO has a second (minor) channel that generates an organic nitrate (3) and removes both HO_x and NO_x radicals:

$$RO_2 + NO + M \rightarrow RONO_2 + M \qquad [R12]$$

Similarly, reactions among the peroxy radicals can act as a key termination step for HO_x radical cycling,

$$HO_2 + HO_2 \ (+M) \rightarrow HOOH + O_2 \qquad [R13]$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \qquad [R14]$$

In pristine regions, where peroxy radical lifetimes are longest, the importance of unimolecular reactions for some specific RO_2 is increasingly being recognized. One such reaction involves isomerization of a hydroxy-peroxy radical derived from isoprene, a process that increases OH concentrations in low-NO_x regions (4). The key processes involved in tropospheric chemistry, from the perspective of HO_x cycling, are summarized in **Figure 1**.

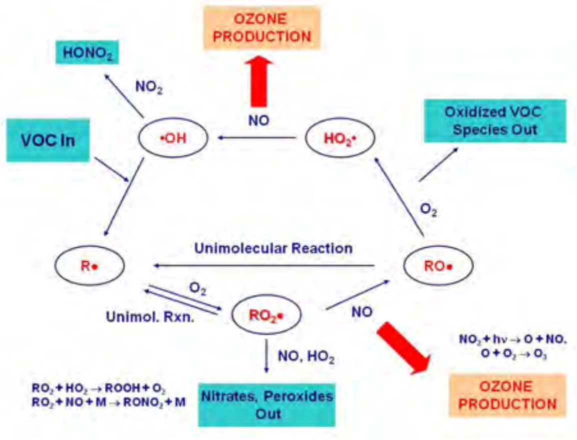

Figure 1. *Key processes involved in cycling of the HO_x/RO_x family in the troposphere.*

Measurement methods

Quantifying ambient peroxy radicals (and their HO_x family member, OH) is challenging because of their low abundances, short lifetimes and spatial and temporal non-uniformity. Techniques available for measurement of ambient HO_2/RO_2 largely fall into two groups (5). The first involves OH detection by laser-induced fluorescence. Here, OH is either determined directly by quantifying the fluorescence observed after laser-induced excitation to its first electronic excited state. Alternatively, the sum of $HO_2/RO_2/OH$ can be detected after chemical conversion to OH *via* addition of NO to the instrument inlet ([R8], [R11], and [R7]). In the second technique, each peroxy radical is converted to more than one product species (NO_2 or HSO_4^-) *via* a chain reaction in the inlet of the instrument, followed by detection of this product species. As an example, HO_2 can be converted to multiple molecules of NO_2 by adding NO and CO to inlet air, initiating a chain reaction involving [R3] and [R7].

Outlook

Understanding tropospheric ozone production, the Earth's self-cleansing capacity, and related problems in atmospheric chemistry requires quantitative understanding of chemistry involving HO_x, NO_x and VOCs. This understanding comes from a combination of ambient measurements of critical components of the system, laboratory investigations of relevant chemistry, atmospheric modelling, and theoretical studies. Progress emerges from the feedbacks between these endeavours. For example, attempts to resolve disagreements between models and measurements may include checks of instrument calibration and interferences or updates to the model based on targeted laboratory studies. Similarly, discovery of a relevant peroxy radical reaction in a theoretical study may drive laboratory studies to quantify the process, followed by its inclusion in an atmospheric model to assess its importance.

References

1. S. Ball, 'Atmospheric chemistry at night', (ECG Environmental Brief No 3).
2. J. J. Orlando, G. S. Tyndall, *Chem. Soc. Rev.* **41**, 6294 (2012).
3. J. Arey, S. M. Aschmann, E. S. C. Kwok, R. Atkinson, *J. Phys. Chem. A* **105**, 1020 (2001).
4. J. Peeters, T. L. Nguyen and L. Vereecken, *Phys. Chem. Chem. Phys.* **11**, 5935 (2009).
5. E. C. Wood, J. Charest, *Anal. Chem.* **86**, 10266 (2014) and references therein.