ROYAL SOCIETY OF CHEMISTRY | ENVIRONMENTAL CHEMISTRY GROUP

January 2019

ECG *Bulletin*

Contaminated Water. This edition features the latest advances and challenges in arsenic contaminated groundwater, a book review by Glynn Skerratt, and an overview of passive sampling for Emerging Organic Contaminants, by Jamie Harrower.

Environmental Briefs. Steve Thornton discusses contaminated water remediation strategies, and Michael Rivett explains the complex risks posed by light non-aqueous phase liquid spills – such as petroleum.

Updates. New findings by Arce *et al*. that bees show a preference for low-levels of neonicotinoids. Fidra work to establish controls on the use and release of nurdles. A recent forum on environmental nanotechnology is summarised.

Also in this issue. Clare Topping and Glynn Skerratt disseminate our CPD member survey. Roger Reeve tells us about his career. Rowena Fletcher-Wood reviews books on phosphates and science communication, respectively. Upcoming meetings include *Plastics, Environmental Matrices*, and *21st Century Chemistry: Disposing of our Nuclear Legacy*, the 2019 Distinguished Guest Lecture provided by Professor Melissa Deneke (University of Manchester).

Contents

Cover image: *Contaminated water with swimming leaf.*
Credit: SusaZoom/Shutterstock

ECG *Bulletin*

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The ECG Interview: Roger Reeve

Dr Roger Reeve is a committee member of the Environmental Chemistry Group. His career started within pollution control in the manufacturing industry and later moved into university, teaching environmental chemistry and chemical analysis. He has recently retired.

What inspired you to become a scientist?

I always had a fascination to find out how things worked. This fascination developed through my school days looking at our world, seeing its complexity and its inherent beauty.

How did you come to specialise in environmental analysis?

My first job focused on research within a process plant for the manufacturing industry. In particular, I specialised in emission control technology. Sulphur dioxide from coal fired power stations was the major concern at the time, whilst serious concern over carbon dioxide was still twenty years away. Design of the processes involved process monitoring and so did the environmental analysis. My academic position combined the two aspects teaching environmental chemistry and analysis.

Could you describe your current position?

My recent retirement means I have more time to pursue my wider environmental and analytical interests. I am currently organising two symposia and a workshop and look forward to other opportunities becoming available in the future.

What advice would you give to anyone considering a career in environmental chemistry?

Being able to move with the times. Many of the current environmental problems weren't even dreamt of at the start of my career, and instrumental analytical chemistry, which I specialised in, was still in its infancy. On the other hand, issues such as clean energy production were relevant then and still are today.

What are some of the challenges facing the environmental chemistry community?

Almost all major improvement in the environment is long term – problem recognition, developing possible alleviation methods, necessary changes in legislation, and ensuring that, in the long term, these changes in legislation are not diminished or removed. Media and funding are often focussed on currently perceived problems. How often is the ozone hole mentioned nowadays, even though it is taking more than a lifetime to repair?

What is the most rewarding aspect of your career so far?

Everyone in education is carried through life by seeing their students develop and succeed, sometimes often way above their expectations. I set up an annual regional schools competition 28 years ago, enjoyed by all, which is still thriving to this day; I wrote an environmental analysis text book which, on publication, turned out to be very popular. I feel privileged to have had a career in an area which has been of so much interest to me.

If you weren't a scientist what would you do?

My history teacher suggested I followed his subject, perhaps because of my wish always to understand and analyse information. I don't think there would have been too much of a career for me in it. Later in life, I have realised the importance of communication but I only master this in subjects I am passionate about.

And what do you do when you are not working?

My environmental and analytical interests are no longer classable as 'work'. I am involved in the Methodist Church. Charity work particularly includes supporting overseas students to continue their education in the UK. I enjoy making home-brew beer, mustard and stained glass art-work. I like cycling, but only in fair weather!

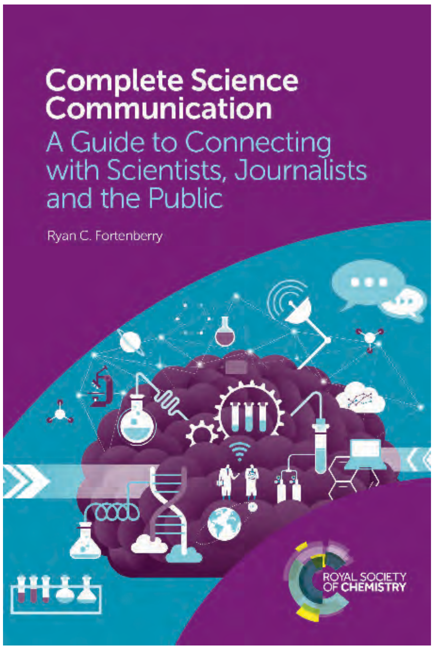
Book Review

Complete Science Communication

Rowena Fletcher-Wood (Science Oxford, rowena.fletcherwood@gmail.com)

Complete Science Communication (*1*), by Ryan C Fortenberry provides a structured and well-written guide for university science communication courses, and includes a collection of high quality model assignments. The scope covers writing (both technical and non-technical), presentations (talks and posters), and public relations.

The text includes nuggets of science communication wisdom that invite the reader to reflect upon the field. The author focuses on the importance of thorough audience foreknowledge and expectations. Ask yourself, he says, "What does my audience already know? What would I like for them to find out?" He expands his analysis to examine our ability to "code switch" – to communicate with different audiences and using different media, and points out potential pitfalls. For example, questions are often used for titles or openings, but these can be counter-effective if the audience's answer is "No". Examples specific to chemistry include the challenge of linguistic barriers and how geochemists and biochemists relate to each other.



Whilst Fortenberry clearly outlines his audience, he does not outline his scope as clearly. Fortenberry interprets "science communication" only as it pertains to universities, and science communication outside academia is never mentioned. As such, the title and even the introduction are misleading – the book is not a complete view of science communication, but a limited and skewed one. A significant proportion of the book consists of information such as the research paper review process, public relations, and the challenge of reproducibility of scientific results. These explanations provide a concise and useful guide to university dissemination processes, but are not always science communication, nor science.

The text also lacks some critical balance: Fortenberry advises scientists to write like journalists, alluding not to the typical but the model journalist and never critiques any part of their role in information dissemination. He defends blunders like weekly "cure for cancer" stories as a natural misinterpretation of the incremental nature of breakthroughs in research.

Fortenberry presents a set of highly specific rules for best practice science communication (poster presenters should have 30s, 60s and 3 min pitches; use a picture for anything that takes more than 10 words to describe), but breaks many himself. Some rules can be extended *ad ridiculum* – such as "the higher the citation to word ratio, the better". Elsewhere, he moderates earlier advice such as advocating information density by then providing guidance on cutting content. Furthermore, many of the most important communications challenges are soft skills. There is barely a mention for how to initiate a conversation, stand confidently on stage, weave your lecture into a story or project your voice. More crucial is the absolutely erroneous advice that presentations are optimal with white backgrounds and black text. Research into human visual processing (*2*) has shown that light grey text on a navy background or the reverse is significantly easier on the eye, especially for those with visual impediments.

Summary

Complete Science Communication is an account of the personal science communication experience of its author. It does not cover a wide scope of science communication and gaps emerge in what it does encompass. However, it does provide a thorough resource of lesson plans and assignments to inspire and support the university-based science communication educator.

References

1. *Complete Science Communication*, Ryan C Fortenberry ISBN: 978-1-78801-110-5, Royal Society of Chemistry, Cambridge, UK, 2018 www.rsc.org/books

2. World Blind Union PowerPoint Guidelines, World Blind Union Low Vision Working Group (2007) www.rnib.org.uk/sites/default/files/WBU%20visual%20presentations%20guidelines.pdf

Book Review

Innovative Materials and Methods for Water Treatment: Solutions for Arsenic and Chromium Removal

Glynn Skerratt (Environmental Consultant, glynn@skerratt.com)

The widespread presence of many arsenic (As) and chromium (Cr) species in the environment, and the need to ensure acceptably low concentrations of both elements in water underlines the importance of this book.

The multiple oxidation states exhibited by both As and Cr in the aquatic environment make for complex toxicological problems and pose significant challenges in effectively and efficiently reducing them to safe levels. This text provides a summary of the underlying chemistry and both current and future technologies that may be employed for the attenuation of their environmental impacts.

In this compilation, the book's four editors merged the efforts of over 50 contributors. Inevitably, this leads to a mixture of writing styles and emphases between chapters and, as a consequence, the book suffers from a lack of overall coherence. Some chapters have a narrow focus; others are more widely relevant.

In Part 1, the book introduces the problem of As and Cr contamination and associated human health issues. Chapter 1 discusses the background solution chemistry of both elements extensively, whilst Chapter 2 contains a rather laboured account of the geochemical and human issues surrounding the problem of trace As contamination in groundwater. Chapter 3 explains the structural effects on red blood cells induced by Cr(III) and Cr(VI); and Chapter 4 includes generic description of the design, development and commissioning stages of an operational plant, and a detailed explanation of the authors' views and experiences of the implementation of these technologies. However, those requiring specific information would need to look elsewhere.

Part 2 reviews innovative materials available for the removal of As and Cr. Chapters discuss metal-based inorganic adsorbents, nanoparticles, metal oxide-doped natural materials, polymeric sorbents, solvent-impregnated resins, ion exchange sorption processes, and water-soluble polymers used in conjunction with membranes. Chapter 12 is devoted to the use of low-cost absorbents for As and Cr removal (*e.g.* fly ash, steel-making slag, red mud, assorted sludges, carbon slurry, and agricultural byproducts), and also contains a detailed description of the various sorption removal mechanisms.

Part 3 describes a number of innovative As and Cr removal techniques (*e.g.* solar-assisted advanced oxidation) and particular applications (*e.g.* As removal from groundwater and wastewaters from geothermal plants). Interestingly, in Chapter 20, the authors discuss combinations of different membrane systems or membranes coupled with more conventional removal methods, whilst in Chapter 21, concentration and electromotive-driven processes such as dialysis and electrodialysis are considered.

The final part presents case studies describing As removal from drinking water and mining effluents in Latin American countries, and As and Cr removal technologies for drinking waters in the USA.

Overall, the book would have benefitted from a more thorough proofreading to correct several minor grammatical and textual errors, and more radical editing to provide a clearer narrative arc for the curious, but not over-specialist, reader. My lasting impression is that this is a book best dipped into rather than a gripping read enjoyed from cover to cover.

Reference

Innovative Materials and Methods for Water Treatment Solutions for Arsenic and Chromium Removal, Editors: M. Bryjak, N. Kabay, B.L. Rivas & J. Bundschuh, CRC Press/Balkema, Leiden, The Netherlands, 2016

Book Review

Phosphates in Soil

Rowena Fletcher-Wood
(Science Oxford, rowena.fletcher-wood@scienceoxford.com)

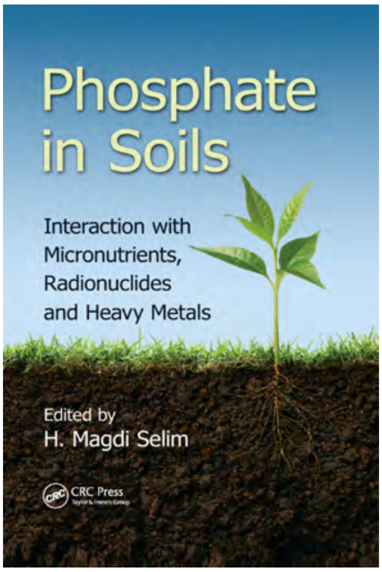
A well-written, clearly laid out book covering the latest advances in phosphate chemistry in soils, including pathways, policy and remediation strategies, health effects, costs, and potential environmental hazards.

Key facts in the book are clearly identified and highlighted, indicating a strong editorial hand. There is a natural progression through the chapters, suggesting it was intended for reading in its entirety; the first three chapters, for example, serve as an extended introduction to phosphate science. Internal references and repeated introductions also make piecewise reading possible.

It is not easy to identify the intended audience for this book. Some concepts (*e.g.* equilibrium constants, normally covered in the chemistry A level syllabus) start at a basic level, for a reader without prior knowledge. Key terms such as heavy metal(loid) are defined from the outset, but elsewhere in the book, in-depth geological and technical knowledge is assumed. Analytical and experimental techniques of some complexity are introduced without explanation and sometimes without accompanying results. An overview of these techniques, their strengths and limitations, would ultimately underpin the discussion. More graphs would also help to visualise the concepts described.

This book makes a brave attempt to collate findings relating to phosphate and trace elements in the hugely complex and messy system of soil solutions.

An impressive array of mineral phases are recognised, but the assumed understanding of them varies from chapter to chapter, with chemical formulae and shorthand names provided in some cases but not in others, and no mention of their crystallography or morphology, despite the contribution of sites to selective metal sorption. Notably, the short name HA is introduced for hydroxyapatite, where HAP, another common abbreviation in the literature, is not. Through robust referencing throughout, the book very much leaves it up to its reader to do much of the footwork to fully understand the concepts conveyed. Despite this, the book's scrutiny of mathematical models and experimental methodologies is thorough; assumptions, strengths and limitations are researched and assessed even where methodologies are infrequently reported in the literature. In particular, field versus pot studies are compared.



Despite its title, the focus of this book lies on trace metal dynamics in soils, their bioavailability, and the effect of changing phosphorus concentrations on their mobilisation. The book mainly addresses phosphorus-mediated remediation of radiological and heavy metal soil contamination and mobilisation of micronutrients, while more space could certainly be given to the comparison between phosphorus-free mechanisms and phosphorus-inclusive ones.

Summary

This book makes a brave attempt to collate findings relating to phosphate and trace elements in the hugely complex and messy system of soil solutions. Whilst affinity sequences can be established, intricate factors such as co-contamination, speciation, daughter species, phosphorus release rates, site competition, varying exposure times the mutual effects of pH on phosphorus and phosphorus on pH make quantification complex.

The book seems best aimed at a seasoned researcher with expertise pertaining only to one chapter, who wishes to broaden their understanding of their field and has time available to read and trace sources.

Reference

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Article

RSC ECG Continuing Professional Development (CPD) survey

Clare Topping (Northampton General Hospital, clare.topping@gmail.com) and Glynn Skerratt (Environmental Consultant, glynn@skerratt.com)

Earlier this year we sent a survey out to Environmental Chemistry Group members to gauge their interest in continuing professional development (CPD) resources. We asked how much CPD training they currently undertake, and whether and to what extent they would like support from the Environmental Chemistry group in this area.

As scientific professionals, we understand the importance of engaging in continuing professional development throughout our career. It incentivises us to engage in lifelong learning and helps us mature into ever more competent professionals, equipped to apply new knowledge, skills and expertise to our work. Undertaking CPD, and being seen so to do, sets an example to professional colleagues and encourages them to do likewise – a virtuous circle.

As a consequence, many professional bodies, including the RSC, require individuals who have achieved chartered status to make a commitment to continuing their professional development as a condition of retaining their chartered designation. In most cases, this means keeping an activity record together with reflective statements about how, and in what way, that element of CPD has benefitted you. Importantly, CPD records often include statements about how the professional will make use of their new insights or knowledge and in the betterment of their work, betterment of their colleagues and advancement of their professional community. An individual's CPD record is sometimes called in for audit by the professional body to make sure that it aligns with their requirements and to provide feedback to ensure that it represents a useful resource to the author and a valuable record of progress over time.

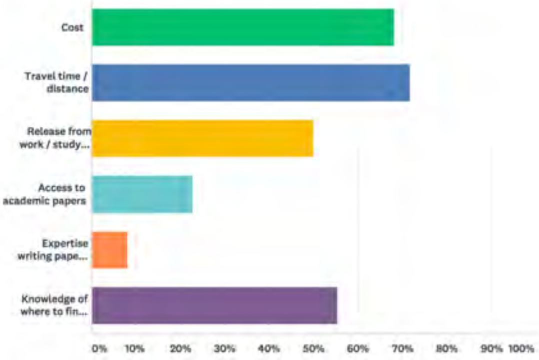
The main barriers to members accessing CPD were cost, time, distance, and knowing where to find resources.

The RSC has its own designated chartered status – the Chartered Chemist. It also holds licences to award Chartered Scientist and Chartered Environmentalist. Maintaining a CPD record is a requirement for each of these to enable you to maintain chartered professional status. There are also Registered Scientist and Registered Science Technician designations with similar requirements.

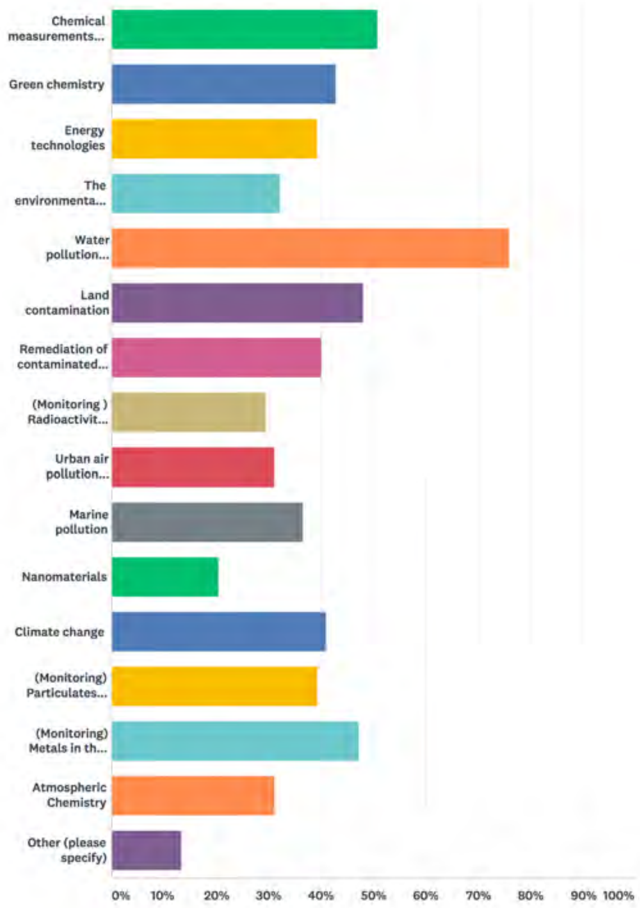
Returning to our survey, we received over 150 responses to the survey, of whom nearly two thirds already hold one or more charterships. Of those who are not chartered, half were hoping to achieve chartered status within the next three years. As such, CPD was a key concern to a large portion of survey respondents.

Half of our respondents currently perform some form of CPD, the most popular resources being webinars, conferences, online articles and papers, and other forms of private study, with online articles deemed the most beneficial resource. A further third of respondents who don't currently undertake any form of CPD, have indicated that they would like to do so.

The overwhelming majority of respondents told us that they would like us to signpost them to CPD resources and to provide our own. The main barriers to members accessing CPD were cost, time, distance, and knowing where to find resources. As a first step, the ECG Committee is investigating ways to signpost useful online content to members, but we are also starting to plan some trial webinars for 2019. The topic of most interest to members was water pollution



Question 11 responses: Which, if any, of these are a barrier for you when accessing CPD resources?



Question 12 responses:. Are there any subject areas that ECG might offer or compile that would be of particular interest to you for your CPD?

chemistry, with other topics such as land contamination and pollution measurement and analysis also attracting significant interest. This information will inform the subjects of our initial webinars, although we are open to further suggestions. Details of webinars will be distributed once topics and speakers have been established.

According to our survey, Massive Open Online Courses (MOOCs) are not currently used by many of our members. These courses are often free to access (although many do offer a certified course for a small fee) and can offer a useful way to gain an introduction to a new topic. A number of platforms host MOOCs; the best known providers are edX (www.edx.org), Coursera (www.coursera.org) and FutureLearn (www.futurelearn.com).

Some of the courses have defined start dates, whilst others are self-paced. Most have online assessments; those that have defined start dates also usually have online moderated discussion forums. All include a course length, suggested study hours per week and a syllabus in their advertisements. Wageningen University, for example, offer courses relating to fossil fuels and biorefineries through edX, whilst Coursera hosts a very popular Pennsylvania State course ‘Creativity, Innovation and Change’. Other interesting courses offered online for free through the three sites mentioned previously include ‘Making Sense of Climate Change Denial and Energy 101’, ‘Blockchain in the Energy Sector’, and ‘Citizen Science, From Data to Action’.

Additional Resources

For those looking for further resources, the Chemistry World website (www.chemistryworld.com) also has some on-demand webinars whilst the RSC has its own YouTube channel which includes some short videos for use in education and outreach as well as the longer ChemCareers webinars available to watch on demand. There are also RSC webinars hosted by the RSC Consulting Group.

Meeting Report

Future Perspectives on Environmental Nanotechnology

David Owen (david.owen@treatchem.org.uk), and Rowena Fletcher-Wood (Science Oxford, rowena.fletcherwood@gmail.com)

This one-day meeting, jointly organised with the journal Environmental Science: Nano, was held at Burlington House, London, on Monday 8th October, and attracted more than fifty delegates from academia and industry.

The morning session, introduced by **Simon Neil**, Executive Editor of Environmental Science: Nano, began with a talk by **Professor Peter Vikesland**, Virginia Polytechnic Institute and State University and chair of the journal's editorial board. He spoke on the application of nanotechnology to better understand the mechanisms behind chemistry in microenvironments, including, but not restricted to, single cells and biofilms. One case study involved the development of nanoprobes to measure pH anisotropy across single, isolated aerosol droplets. This was performed through the implantation of coated gold nanoparticles into an aerosol droplet, followed by the use of highly focussed spectrometry to track the degree of the particle's ionisation. Bifunctional materials such as 4-aminophenol were used for the film coating.

This was followed by a talk on the development and assembly of multifunctional graphene oxide for advanced filtration and photolytic water treatment by **Professor John Fortner**, Washington University in St. Louis. His work explored the controlled treatment of graphene oxide to form a three dimensional nanomaterial, the morphological equivalent of a balled up sheet of paper. This pseudo-particulate material can be attached to a supporting filtration substrate film to produce a monolayer. Subjected to various foulants, including biological species like *E. coli*, crumpled graphene oxide (CGO) matrices outperformed various commercial ultrafiltration membranes and demonstrated enhanced resilience under chemical cleaning conditions. By encapsulating TiO_2 nanoparticles, CGO photocatalytically degraded methyl orange. Magnetic iron, silver and gold nanoparticles have also been encapsulated.

The audience rated the event an 8.6/10 for the quality of the speakers and 39% said it surpassed their expectations

Other talks included that by **Dr Xianjin Cui**, University of Birmingham, who showcased the Facility of Environmental Analytics and Characterisation's services available at Birmingham for the characterisation of small terrestrial and freshwater samples including environmental nanoparticles. **Dr Rowena Fletcher-Wood** then introduced the science education company *Things We Don't Know*, an online science magazine that focuses on explaining the questions to which science still seeks answers, supporting research crowdfunding, cataloguing ongoing research questions, and providing real time science news updates from researchers.

Dr Gregory Lowry, from Carnegie Mellon University, opened the afternoon session, speaking on the application of nanotechnology in agriculture. His work focuses on delivering nanoparticles into plants to perform vital functions such as improved nutrient absorption, fungal resistance and photosynthesis under salt stress whilst avoiding the complications of overspray and excess runoff. His research demonstrated the introduction of modified biomolecular nanoparticles into stomata, and subsequent transport of these materials throughout the internal plant structure. Further work explored optimal delivery methods, and patents on these methods are currently being filed.

Deriving nanoparticulate alumina via the controlled hydrolysis of aluminium nitrate, **Dr Wei-Guo Song**, Chinese Academy of Sciences, discussed the application of this material for environmental arsenic sorption, and proposed a mechanism for its action: a surface cation exchange reaction, whereby arsenic permanently adheres to external hydroxyl groups. Ongoing research is investigating the action of other metal-based nanomaterials, including Fe, Ce, FeOOH, Al_2O_3 and $MgSiO_3$, and the removal of other contaminants including Pb and U.

Dr Heather Au, Queen Mary University of London, described her work on the hydrothermal carbonisation of sugars at sub-generated pressure to form new building blocks for organic reactions, including fuel materials. Her work includes the study of carbon dots and cross-linked hard and soft carbon. Dr Au's talk focussed on her research into a sodium equivalent to the lithium ion battery. The basis of this is that sodium salts exist in greater quantities in nature and if the technical issues of electrical capacity can be optimised (the theoretical capacity is 300 milliamps, but this number is not well justified), a more eco-friendly battery could be produced. Much of the research was directed at optimising the carbon used for intercalating sodium ions in a nanoporous network, and exploring the underlying mechanism for this storage. Research challenges highlight that the ability to get the correct carbon quality greatly affects the degree of efficiency of charge that can be stored and delivered as a working battery.

Dr Jerome Rose, European Centre for Research and Teaching, presented his research into the life cycle analysis of nanomaterials syntheses – an international project that modified nanomaterial design strategy to produce safer, more environmentally friendly technology. His work revises existing risk assessment protocols to prevent release of rogue materials.

The symposium was closed by **Professor Joel Pedersen**, University of Wisconsin-Madison, whose research focuses on coating inorganic nanoparticles with organic materials to facilitate their insertion into lipid bilayers. He demonstrated that a complex sequence of reactions are required to explain the mechanism behind insertion, and that future efforts aim to unweave these underlying mechanisms to harness this technology for applications in drug delivery.

The audience rated the event an 8.6/10 for the quality of the speakers and scientific content, and 39% said it surpassed their expectations.

Article

Global plastic pollution: the impact of 'nurdles'

Madeleine Berg (Fidra, madeleine.berg@fidra.org.uk)

Plastic pollution has risen exponentially since the material entered widespread use in the 1950s. By 2015, global production had increased to 381 million metric tons per year (*1*) and 8 million metric tons are estimated to enter our oceans annually (*2*). Fidra is an environmental charity working with retailers, industry and the scientific community to reduce plastic waste and pollution in our seas. They focus on a source of pollution that is relevant to almost all plastic products: pre-production plastic pellets, also known as "nurdles".

Plastic pellets, powders and flakes are used to make virtually all our plastic products. These microplastics, usually around 2-3 mm in size, are found on beaches worldwide. In the marine environment they look like fish eggs, and thus are frequently consumed by marine wildlife, including puffins (*3*), the common gull (*4*) and fulmars (*5*). Once trapped in their stomach, the pellets inhibit appetite and deprive marine species of the energy required to forage, grow, reproduce, and avoid predation (*6*).

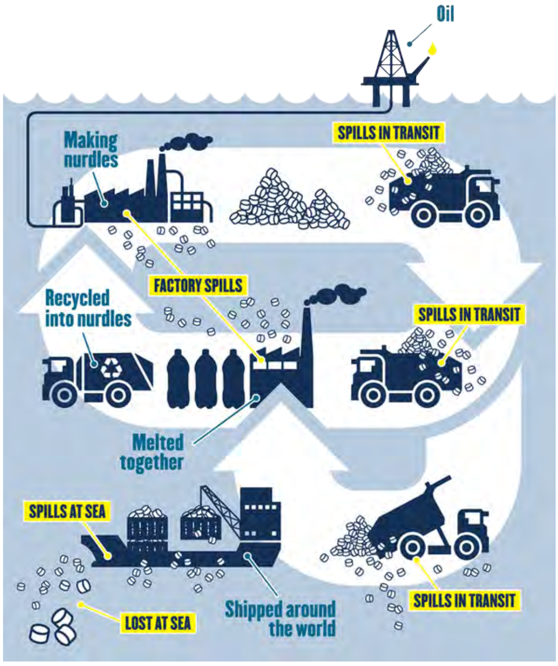
Pellets are used as an indicator of seawater pollution levels around the globe (*7*). Persistent organic pollutants (POPs) from the surrounding seawater adsorb onto the surface of pellets, concentrating toxins to levels millions of times higher than surrounding water (*8*). In addition, chemical additives used during manufacturing, such as plasticisers, flame retardants and colourants, can leach out into seawater (*9*), from where they may be absorbed by marine species before or after ingestion (*9–11*). Pollutants concentrate up the food chain and impact the health of marine wildlife (*12*).

In 1990, the American Chemistry Council and the Plastics Industry Association (formerly SPI) created a scheme called Operation Clean Sweep that encourages companies to identify areas at risk of spills and apply best practice measures to achieve zero pellet, powder and flake loss into the environment. Spills can happen wherever pellets are handled – from production to storage to recycling facilities, at loading tankers or transport containers. Spilt pellets can then enter drainage systems or get washed into nearby waterways by wind and rain, ultimately ending up in our oceans. Spills not only impact the environment: they also decease operational efficiency, cause slips and falls, and affect sustainability.

Operation Clean Sweep is now endorsed by The British Plastics Association and Plastics Europe, and information may be found on the British Plastics Federation website (*13*).

Nurdles on a beach at North Queensferry in the Firth of Forth, Scotland. There are estimated to be several million of these pellets on this beach alone.
Photo: Alasdair Neilson

A close up of pellets found on the Firth of Forth in Scotland – each pellet is 2-3mm in diameter.
Photo: Melanie Pyne



This infographic shows the supply chain of the plastics industry and where spills might occur – © Fidra

However, whilst some companies have made significant strides to manage this problem, across the board uptake of the scheme has been low. Furthermore, it does not grant companies the opportunity to demonstrate their efforts to customers. As such, Fidra is advocating the use of standards and certifications to improve traceability and transparency along the supply chain. This would not only boost uptake of best practice, but also provide the customer with the confidence that the pellets, powders or flakes used to make their plastic product have been handled responsibly at every stage. This approach is supported by industry representatives from across the plastics supply chain.

Fidra is currently in consultation with stakeholders designing a solution fit for purpose. For more information on Fidra's work or to get involved, please contact madeleine.berg@fidra.org.uk.

Fidra also runs The Great Nurdle Hunt project (14).

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Article

Arsenic contaminated groundwater - A problem in India and the UK

Dominik Weiss (Imperial College London, d.weiss@imperial.ac.uk), Jay Bullen, Hany Heiba, Andreas Kafizas, Tony Cass, Ramon Vilar, Peter Childs, Stephen Skinner (Imperial College London), Pascal Salaun (University of Liverpool), Priyanka Mondal, Swachchha Majumdar (CSIR-Central Glass and Ceramic Research Institute)

The identification of arsenic (As) as a potent carcinogen led the World Health Organisation (WHO) in 1993 to revise their guidelines for maximum As content in drinking water from 50 µg/L to 10 µg/L. Today, an estimated 120 million people throughout the world are exposed to unsafe levels of As in their drinking water.

Arsenic naturally occurs in shallow groundwater aquifers in many countries. India and Bangladesh are among the worst cases, where concentrations of up to 1000 μg/L have been reported (*1*). With respect to India, arsenic poisoning from drinking water is on the rise, with reports of new cases from the North Eastern states and the Ganga-Meghna-Brahmaputra plain in Bihar, from the states of Uttar Pradesh and Jharkhand in the Gangetic plain, and from the state of Assam in the Brahmaputra plain (*2*). In West Bengal, the worst affected Indian state, the estimated number of unsafe tube wells in eight of the most affected districts is 1.3 million, and the estimated population drinking arsenic contaminated water above 10 and 50 μg/L are 9.5 and 4.2 million, respectively. About 8% of the Indian population is under the threat of arsenic poisoning (*3*).

The challenge associated with contaminated groundwater, however, is not restricted to India. More than 85,000 private water supplies in the United Kingdom supply water to ~1% of households. In 2011, the Drinking Water Inspectorate reported that 3% of private wells studied contained arsenic at levels above present maximum contaminant level of 10 µg/L. Between 2011 and 2013, commissioned by the UK Health Protection Agency, the British Geological Survey undertook a sampling campaign of 512 properties in Cornwall served by private water supplies. Results from the study showed that five per cent of drinking water samples collected exceeded 10 µg/L arsenic concentration (*4*).

Arsenic poisoning from drinking water is on the rise in India

Figure 1. *The Arsenic Removal Plant presently used by the CGCRI used in rural areas in West Bengal. The ATP combines adsorption on iron oxide and ultrafiltration using a ceramic filter.*

Arsenic treatment plants (ATP)

Access to drinking water in rural and remote areas away from an official water supplier requires tube wells. The ideal solution is to reach a non-contaminated deep aquifer, but that is often not economically feasible. Currently, there are about five million tube wells fitted with hand pumps in West Bengal, and more than 12 million tube wells in Bangladesh that provide drinking water from a depth of 15-60 m (*1*). Simple and small-scale systems to remove the arsenic at the point of collection are primarily based on fixed bed columns. However, difficulties with respect to operation and maintenance of these smaller units have emerged during field trials and frequent monitoring of arsenic levels would be required to guarantee safe operation. In addition, purification and sludge management is difficult and poses another form of hazard. Consequently, arsenic treatment plants with larger capacities are being developed.

Various ATP designs have been tested, including ion

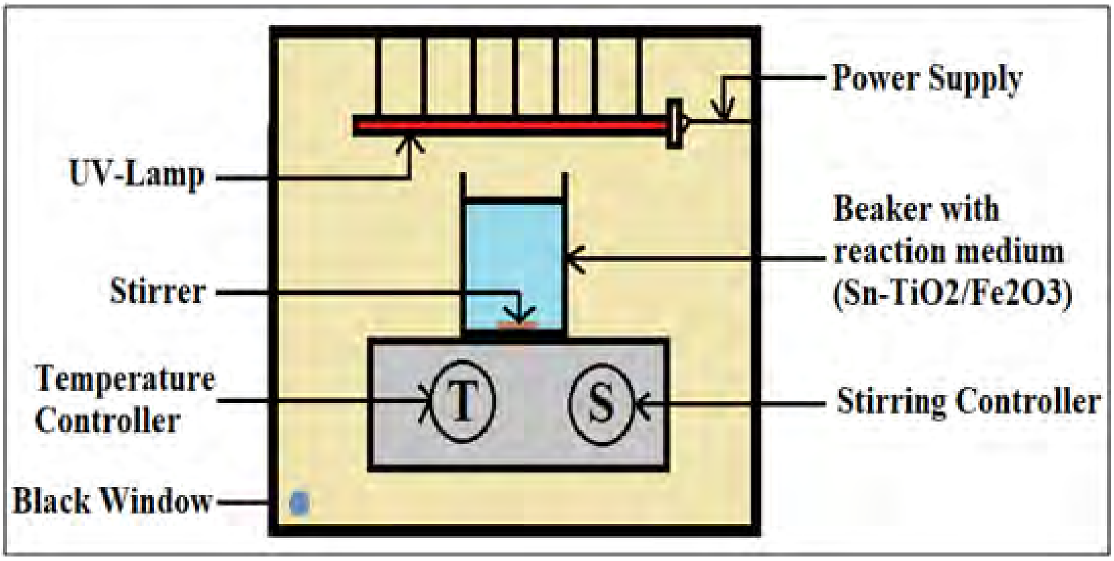

Figure 2*. A schematic diagram of the reactor used at Imperial College London to develop and test efficient photocatalytic oxidation of As(III) to As(V) in contaminated groundwater (unpublished, Hany Heiba).*

exchange, adsorption, ultrafiltration, reverse-osmosis, and adsorption-precipitation by metals (predominately ferric chloride) followed by coagulation (**Figure 1**). Chemical treatment and adsorption have emerged as the most effective solution, but fundamental challenges remain. This is reflected in a critical evaluation of the efficiency of ATP projects in removing arsenic from raw groundwater: a 2-year-long study, covering 18 ATPs from 11 manufacturers, installed in an arsenic affected area of West Bengal (*5*). Concentrations as high as 364 μg/L were found in the filtered water, and none of the ATPs could maintain arsenic in filtered water below the WHO provisional guideline value; only two could meet the standard value of 50 μg/L throughout. Furthermore, standard statistical techniques showed that ATPs from the same manufacturers were not equally efficient. Efficiency was evaluated based on point and interval estimates of the proportion of failure. The outcome was that many ATPs were identified as simply not fit for purpose.

Arsenic occurs in its inorganic form as oxyanions of the trivalent arsenite, As(III), or pentavalent arsenate, As(V), in the aquatic environment

The challenging groundwater in West Bengal and the need to oxidise arsenic to improve removal

The Indian government, NGOs, and international organisations have made great efforts to reduce arsenic exposure. The most successful program thus far has been the construction of deep tube wells and the testing of several millions of wells, which has led to a significant proportion of the affected population to switch from unsafe to safe wells. Unfortunately, with the high percentage of affected tube wells, the possibility of switching is limited. In some districts, depths of more than 180 m are required to reach brown sediments, and there is often a narrow depth range where arsenic concentrations are low while manganese concentrations and salinity are not too high (*1*).

In regions with limited options for alternative water sources, optimisation of water treatment remains urgent. The simplest method takes advantage of naturally present dissolved Fe(II), by co-precipitation of arsenic with hydrous ferric oxides that are formed within 15-60 min when pumped groundwater encounters air. Hydrous ferric oxides (with sorbed arsenic) are removed by settling or filtration through sand. However, studies have shown that the natural iron concentrations in many affected regions are too low to remove more than 50% of the arsenic.

Arsenic occurs in its inorganic form as oxyanions of the trivalent arsenite, As(III), or pentavalent arsenate, As(V), in the aquatic environment (*6*). The distribution between As(III) and As(V) in water depends critically on the redox environment and pH (*6*). Under typical anoxic groundwater conditions at near neutral pH of 7, As(III) is the predominant form of arsenic, which is far more toxic and mobile than As(V). Arsenite has low affinity to mineral surfaces, while arsenate adsorbs easily to solid surfaces, such as natural or synthetic metal oxides (*7*).

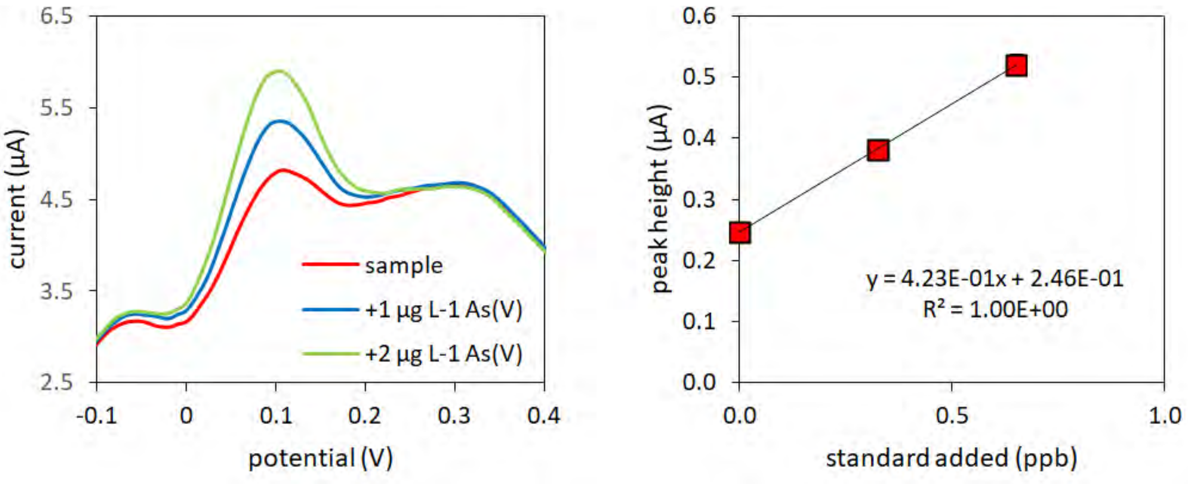

Figure 3. *On site electrochemical determination of total arsenic using stripping voltammetry with a gold electrode and the method of standard additions (17). (unpublished results, Jay Bullen).*

High concentrations of As(III) and high phosphate and silicate concentrations create added challenges for arsenic removal. As(III) sorbs weakly on iron oxides at circumneutral pH (pH 6.5-7.5) and is out-competed by the strongly sorbing phosphate and by weaker sorbing but abundant silicate and carbonate. Therefore, efficient arsenic removal requires oxidation of As(III) to the strongly sorbing As(V).

As(III) is typically oxidised to As(V) by chemical treatment, but the relatively high cost of oxidants and the formation of toxic by-products are significant drawbacks. Photocatalytic oxidation of As(III) is being investigated as an alternative to chemical oxidation (**Figure 2**). Photocatalytic As(III) oxidation with sunlight leads to significantly higher arsenic removal (40-90%) than precipitation alone (*6*).

The need for monitoring arsenic on-site at the ATP

Arsenic detection has always been challenging, especially on-site (*8*). On-line determination of arsenic in both the inflow and outflow streams in the ATP could provide several advantages. In the first instance, it would confirm whether arsenic levels in the outflow were below the maximum contaminant level and therefore confirm that the system was performing to specification. Secondly, it should be possible to then operate the treatment process dynamically, for example, by adjusting the flow rate or the adsorbent if it were approaching saturation. Additionally it should be possible to then predict when the removal system requires regeneration or replacement and identify early any unexpected failures. Field tests kits, mostly based on colorimetric methods, have been highly criticised for low reliability, time demand, and generation of toxic chemicals (Gutzeit method) (*9, 10*), despite major improvements (*11*). Other standard spectroscopic methods such as fluorescence or atomic absorption (hydride and graphite techniques) show excellent sensitivity. When coupled to chromatography, they are powerful tools for arsenic speciation, but these methods are expensive and laboratory-based, and thus not suited for rural on-site analysis.

Voltammetric methods, which use cost effective, portable, low running cost electrochemical systems, are much more suited for rural on-site analysis (*12*) (**Figure 3**). Although there is an extensive literature on the electrochemical determination of arsenic, primarily using stripping voltammetry (*8, 13, 14*), all methods suffer from drawbacks: those developed on solid electrodes, such as gold disc, usually employ relatively high acidic conditions. More recent methods that use nanoparticles, self-assembled monolayers, biomolecules or synthetic polymers, have a limited/unproven long term stability and often require complex experimental procedures (*e.g.* for the preparation of the sensor surface). Nevertheless, stripping voltammetry remains at the forefront of on-site arsenic analysis, is formally approved, and is utilised by some companies for metal detections (*8*). Commercially available systems, however, tend to have high capital costs and may require technical skills to operate.

> **Voltammetric methods, which use relatively cheap, portable, low running cost electrochemical systems, are much more suited for rural on-site analysis**

The development of a novel generation of ATP

A collaboration between Imperial College London, University of Liverpool and CSIR-Central Glass and Ceramic Research Institute

Important progress in arsenic remediation has been made over the last few years by Imperial College London, the University of Liverpool and CSIR-CGCRI. This research includes the development of mixed mineral oxides (TiO_2/Fe_2O_3), which, in combination with sunlight or a source of ultraviolet radiation, photocatalytically oxidise arsenite to arsenate within minutes without the use of chemical oxidants and the production of toxic by-products (**Figure 2**) (*15, 16*). The resulting As(V) species can then be easily and efficiently extracted by mineral oxides. Progress also includes the development of low-cost electrochemical sensors that accurately determine arsenic concentrations down to the lower ppb level. The aim of current work is to apply these two new techniques to an ATP developed by a team at the CSIR-CGCRI in Kolkata, led by Majumdar and co-workers. This system, patented in three countries (Chile, India and Taiwan) and widely used in rural areas in India, combines the use of an iron oxide sorbent with subsequent micro filtration. We propose to introduce the mixed mineral oxides instead of the iron oxides and to integrate the sensors at the inlet and outlet of the ATP.

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Further Reading

The geology of groundwater arsenic contamination, arsenic speciation, toxicology, and methods of remediation have been the subject of many previous articles in the ECG Newsletter and ECG *Bulletin*. See the following issues: June 1998, January 1999, July 1999, February 2002, January 2003, July 2003, July 2004, January 2006, January 2009, September 2011.

Article

Passive sampling for polar organic contaminants

Jamie Harrower (Glasgow Caledonian University/James Hutton Institute, jamie.harrower@gcu.ac.uk)

The presence of Emerging Organic Contaminants (EOCs) within the environment has drawn a lot of attention in recent years due to their unknown long-term effects on aquatic life and human health. EOCs include pharmaceutical and personal care products and illicit drugs, and their concentrations in UK surface waters have been reported in the range of ngL^{-1} to µgL^{-1}(*1*).

Passive sampling devices are easy to use, require no maintenance and can be deployed in a range of different environments, including sites with limited access

There are numerous sources of EOCs including agricultural run-off, hospital effluent, septic tanks and pharmaceutical industrial plants. However, their main entry route into the environment is from the discharge of effluent from waste water treatment plants (WWTPs). EOCs are polar by nature and have varying physicochemical properties (logK_{ow}, water solubility, acid dissociation constant and vapour pressure). Once discharged into the environment, EOCs can degrade into the corresponding metabolites and therefore partition into a variety of environmental compartments. Robust and widespread monitoring programmes are therefore essential.

Overview of passive samplers

Traditionally the most commonly used sampling technique for river water has been spot sampling as well as 24-hour composite sampling (time, volume or flow proportional). However, spot sampling only provides a snapshot of the concentration of contaminants within the environment and is unable to capture spatial and temporal variations (*2*). Passive sampling devices (PSDs) are proposed as a low-cost and easy-to-use alternative, as they can be deployed in large numbers for much longer periods of time (up to several months)(*2*). Passive sampling relies on the transport by absorption or adsorption of micropollutants from the sample matrix (i.e. the surrounding water) to the receiving phase (the sorbent) driven by the difference in chemical potential between the two types of media (*3*). PSDs can be used to measure time-weighted average (TWA) concentrations for comparatively long time periods (≥ 7 days).

Types of PSDs and advantages

There are many advantages of PSDs over traditional methods. PSDs provide TWA concentrations, are non-mechanical, easy to use and require no maintenance, and can be deployed in a range of different environments, particularly sampling sites which have limited access. As passive samplers concentrate the analytes on the sorbent material, their detection limits tend to be much lower than those in spot sampling.

There are generally two types of passive sampling devices used to measure concentrations of polar organic contaminants: Polar Organic Chemical Integrative Samplers (POCIS) and the Chemcatchers (*3*). The diagram in **Figure 1** illustrates the assembly of a POCIS device. Its main components include a compression ring, a polyethersulfone (PES) membrane and the Oasis Hydrophilic Lipophilic Balance (HLB) sorbent, which has the ability to extract a broad range of polar organic compounds (*4*). The Chemcatcher sampler typically contains a styrenedivinylbenzene adsorbent bound in a PFFE disk (*3*). The membrane material used in PSDs is very important as it acts as a semi permeable barrier between the sorbent and surrounding aquatic environment (*4, 5*). As such, it allows polar molecules to

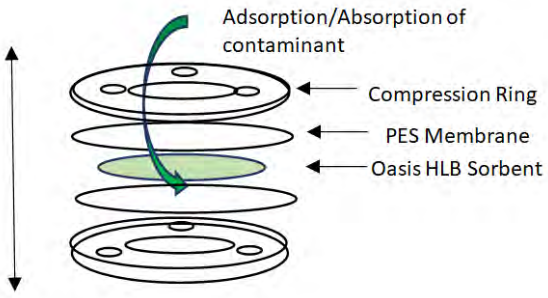

Figure 1. *Schematic diagram of the Polar Organic Chemical Integrative Sampler.*

pass through to the sorbent, while filtering out particulate of diameters greater than the pore size. If the membrane is damaged or compromised, site-specific biases can be introduced in the measurement, leading to reduced uptake of the target compounds as a result of biofouling.

Calibration of PSDs

To quantify TWA concentrations of organic pollutants, PSDs must be calibrated. This involves measuring the sampling rate (RS) of the device, which can be achieved either using a flow-through exposure tank in the laboratory, or by *in situ* calibration (*3*). The latter method is highly recommended for determining an RS value representative of the exact location where future measurements will be made. In comparison to laboratory calibrations, there have been very few *in situ* calibrations performed for organic contaminants, mainly due to the considerable effort they require (*4*). However, it is considered essential for quantitative purposes because it accounts for site-specific factors, such as matrix composition and hydrological conditions, which otherwise could not be replicated under laboratory conditions. Zhang *et al.* (*4*) have shown that RS values for a selected group of endocrine disrupting compounds (EDC) differ between *in situ* and laboratory calibrations. *In situ* calibrations require an extensive equipment set-up, which would need to be maintained. Calibration procedures are also very labour intensive and involve collecting and processing large amounts of both spot samples and passive sampling devices to calculate an average sampling rate (RS) (*4*). Calibrations are usually conducted over a period of 1-2 weeks; once validated, the calibrated RS values can be deployed for field measurements for longer periods.

Measuring pollutants in PSDs

The accumulation of micropollutants in passive samplers can be described by first-order kinetics in which an initial linear phase is followed by a curve-linear and equilibrium phase, as shown in **Figure 2**. This behaviour is described by Equation 1 (*2, 6*):

$$C_S(t) = C_w \frac{k_1}{k_2}(1 - e^{-k_2 t}) \qquad (1)$$

where Cs(t) is the concentration of the analyte in the sampler at exposure time t, C_w is the analyte concentration in the aquatic environment, and k_1 and k_2

$$C_S(t) = C_w k_1 t \qquad (2)$$

are the uptake and offload rate constants respectively (*2, 6*). In kinetic sampling the rate of mass transfer to the receiving phase is assumed to be proportional to the difference between the chemical activity in the water phase to that in the reference phase. The rate of desorption of a chemical from the receiving water in the initial sampling phase is negligible. The sampler works in the linear uptake regime and Equation 1 can be reduced to (*2, 6*):

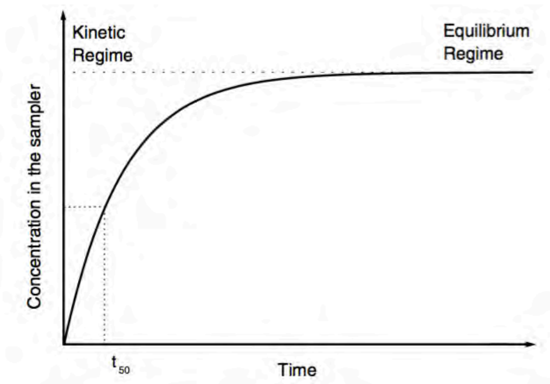

Figure 2. *Passive sampling devices operating in two main regimes (kinetic and equilibrium).*

Equation 2 can be rearranged to give:

$$M_S(t) = C_w R_S t \qquad (3)$$

where MS(t) is the mass of analyte accumulating on the receiving phase at time t, and RS is the sampling rate (typically given in units of Ld^{-1}), which can also be interpreted as the volume of water cleared of analyte by the device per unit of exposure time. When RS is known, CW (i.e. the TWA concentration of the pollutant in the water) can be calculated from the sampling rate (RS), exposure time (t) and the amount of analyte MS(t) trapped by the receiving phase (2).

Factors affecting PSDs

Water flow rates, water temperature, biofouling, salinity and pH all affect the uptake of organic compounds in passive samplers (*7*). The majority of pharmaceuticals entering the environment have acidic hydrogens that can dissociate, forming anion/cation structures. This process is pH dependent, and 50% of the species will be dissociated when pH = pK_a. This implies that pH can affect the sampling rates of contaminants. Li *et al.* (*8*) showed a threefold increase for basic compounds under increasing alkaline conditions in POCIS devices, and a similar decrease for acidic compounds.

The type of membrane used in POCIS devices has also been shown to affect RS values. Zhang *et al.* observed that polyethersulfone membranes returned higher Rs values for EDCs than polysulfone ones (*4*). The surface area of the membrane in a passive sampler has also been shown to affect RS.

Modelling compound uptake

There has been debate about whether RS values can be predicted using the physicochemical values of individual polar organic contaminants. To avoid long calibration periods, ideally RS could be determined using values such as $\log K_{ow}$ and $\log D_{ow}$ (*9*). However, this has not been possible due to the limited amount of field data available on RS. The diverse functional groups which are present in polar compounds and the associated complex interactions that are possible also make modelling the uptake rate very challenging (*10*). Several studies have investigated trends in RS for different alkylated phenols, pesticides and EDCs, but found no significant correlation between molecular structure and RS (*7*).

Chirality of compounds

Another area of research which has drawn particular interest is compound chirality, as approximately half of all drugs available are chiral and exist as enantiomers (*11*). Many stereoselective processes in human metabolism and in waste water treatment plants lead to enrichment of one of the enantiomers in waste water effluent and, consequently, in the environment. In some instances, it has been observed that chiral micropollutants display enantiospecific toxicity (*12*). Future studies should aim towards reporting pollutants with chiral centres at enantiospecific levels to improve monitoring and risk assessments. Presently, passive samplers have not been assessed for determining the enantiomeric distribution of chiral compounds in the environment.

> **Future studies should aim towards reporting pollutants with chiral centres at enantiospecific levels to improve monitoring and risk asssessments**

Preparation, extraction and analysis of PSDs

The traditional method used to measure organic pollutants in river water has been filtration, followed by solid phase extraction (SPE), and then analysis by gas or liquid chromatography coupled with mass spectrometry. In the case of using gas chromatography, a derivatisation step is required. However, analysing the sorbent material of the passive sampler after a deployment period in the environment is slightly different, as there is no requirement of SPE. The sorbent material is removed and extracted using a polar solvent such as methanol, dried down and reconstituted in a suitable solvent and transferred to vials for analysis.

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Update

Neonicotinoids alter food preferences and colony behaviour in bees

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The relationship between neonicotinoid pesticides and pollinator decline has been the subject of a variety of research studies in recent years. These widely-used pesticides are thought to contribute to the observed reduction in the populations of bees and other pollinators because they are applied to areas where bees forage. Residues have been detected in bee-collected pollen and experimental evidence has pointed to a correlation between exposure and bee and colony fitness.

In a recent article Crall *et al*. showed that bees exposed to neonicotinoids spent less time nursing larvae, had an impaired ability to warm the nest and to build insulating wax caps around the colony (*1*).

On 27th April 2018 the EU voted to extend the ban on the outdoor use of three neonicotinoids: Clothianidin, Imidacloprid and Thiamethoxam. These pesticides had already been banned in 2013 for oil seed rape and spring cereal seed treatments as well as winter cereal crop sprays. However, until April this year, they could still be used for sugar beet, in winter cereal seed treatments and for horticultural uses. This latest sanction, unlike the 2013 ban, was supported by the UK government. This recent move by the EU follows a European Food Safety Authority report that found that neonicotinoids posed a threat to all species of bees no matter where or how the chemicals were used in an outdoor environment. However, Thiacloprid and other neonicotinoids remain exempt and all these pesticides can still be used in greenhouses. Furthermore, on 11th October 2018, another neonicotinoid, Sequoia, was authorised in the UK for use in greenhouses. Despite protests from the farming community about the ban in 2013, in December 2017 Buglife reported higher crop yields across the EU since the initial ban (*2*)

> **In previous trials the ability of the bees to detect and avoid neonicotinoids was not assessed**

A previous ECG *Bulletin* (*3*) covered a World Integrated Assessment (WIA) study on the possible detrimental effects on pollinator populations and the impacts on biodiversity and food security, whilst the February 2017 ECG *Bulletin* (*4*) featured interviews with Dr Ben Woodstock (CEH) and Prof Simon Potts (Reading University) giving their views on the role played by bumblebees in pollination and the impact of their decline on food security. This update reviews the results in a recently published paper by Arce *et al*. that looks at the risk that neonicotinoid pesticides are likely to pose to pollinators such as bumblebees (*5*).

Bombus terrestris. Photo: Clare Topping

Using *Bombus terrestris*, one of the UK's six commonest bumblebees and one often bought for commercial crop pollination, as the subject, the authors examined the behaviour of colonies of these bees when exposed to varying levels of neonicotinoids in sucrose solutions. Ten separate colonies were given the option of 0, 2 and 11 ppb (parts per billion) Thiamethoxam in six different dispensers. For ten days they measured how often the bees visited each of the concentrations and how much solution they took. The authors also looked at the behaviour of individually tagged bees over the same time period. Many of the previously published trials only studied the impact of neonicotinoids on bees by feeding them with spiked food; the bees were not given an option of 'no pesticide' and therefore their ability to detect and avoid neonicotinoids was not assessed. The only previous study examining the preferences of bees when given a choice of sugar solution with or without neonicotinoids was conducted over a 24 hour period and showed that, whilst bees could not detect the tested pesticides through their proboscis, individual bees consumed more sucrose laced with pesticides than without (*6*). By continuing the study over ten days, Arce and co-workers hoped to assess the risk rather than the hazard to the bees, i.e. what the likelihood of their exposure would be as well as the likely consequence of exposure. By using colonies, rather than individual bees, the researchers hoped to ensure that they mimicked conditions in the wild by also allowing social cues to be passed between bees. A previous study using different coloured feeders (*7*) showed that as colonies gain experience they can adapt their behaviour to overcome innate behaviours such as colour preferences of flowers.

Bees seem to develop a preference for these chemicals and potentially transmit this preference to the colony

In this study, bees were initially attracted preferentially to either the 0 or the 11 ppb solution over the 2 ppb solution, with correspondingly more of the former solutions being consumed by the bees. Over time, however, the bees preferentially moved to the 2 ppb solution, with fewer visits to the 0 ppb solution. The proportion of visits to the higher concentration remained about the same. Part way through the study, the position of the solutions was randomly changed in case there were learned behaviours and preferences not related to the concentration of Thiamethoxam. However, the trend remained the same with the bees preferring the 2 ppb solution, so it would appear that the foragers could detect the Thiamethoxam and change their behaviour accordingly. This preference increased at approximately 1% per day so that by day 10 there were 28% more visits to the 2 ppb feeders than to the 0 ppb feeders. The studies of tagged bees, which were classed as experienced foragers, also showed the same increasing rate of preference for the 2 ppb solution even though initially they showed a strong preference for the 0 ppb feeder indicating an initial aversion to the Thiamethoxam (42% of visits). As with a previous study by Baracchi et al. (7), this work indicates that the presence of a neonicotinoid gradient alters the attractiveness of the food to bees and that they seem to prefer lower concentrations. In the study by Baracchi et al., bumblebees were deterred by higher doses of neonicotinoids, but attracted to lower doses and more quickly learned to associate these spiked flower feeders with reward. It is suggested that low concentrations of neonicotinoids act in a manner similar to low doses of naturally occurring alkaloids, such as caffeine and nicotine, to provide a memorable psychoactive signal thus acting as a post-ingestive stimulant that can encourage bees to remain faithful to contaminated food sources.

Field of Rapeseed, one of the crops previously treated with neonicotinoids. Photo: Clare Topping

Conclusions

The recent work of Arce *et al*. concludes that the risk that bees will be exposed to neonicotinoids is higher than initially thought from previous trials. They have shown that the bees seem to develop a preference for these chemicals and potentially transmit this preference to the colony. As studies continue, it appears that the impact of these pesticides on bumblebees and potentially other pollinators is more far-reaching and complex than initially assumed.

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ECG Environmental Briefs **ECGEB No 19**

Managing risks from contaminated groundwater using natural attenuation

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Contaminated soil and groundwater can cause detrimental effects to human health, the wider environment and quality of water resources, as well as having major socio-economic impacts. There are many thousands of potentially contaminated sites across Europe where remediation is required, with associated annual management costs that run into several € billion. Common sources of groundwater contamination include releases from industrial facilities *e.g.* chemical manufacturing, processing and storage facilities, distribution and waste disposal facilities, coal mine sites, and agricultural practices. While aromatic hydrocarbons, halogenated compounds and phenols represent the majority of organic contaminants from these sources, inorganic compounds (*e.g.* heavy metals and nutrients) are also important.

Many engineered remediation methods are available to clean-up contaminated sites with the objective of managing associated risks to receptors such as humans, wells, groundwater and surface water. In contrast, natural attenuation (NA) refers to the use of naturally occurring *in situ* physical, chemical, and biological processes which act in isolation or combination, without human intervention, to reduce the mass, toxicity, mobility, flux, volume or concentration of contaminants in soil and groundwater. These *in situ* processes include biodegradation, abiotic degradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction. Monitored natural attenuation (MNA) is the application of NA processes for the management of soil and contaminated groundwater. MNA provides a rigorous performance assessment of NA using appropriate monitoring strategies to demonstrate an acceptable reduction in environmental risk at a specific compliance point or receptor within a reasonable timeframe.

Conceptual model for natural attenuation of hydrocarbons in groundwater

The processes of natural attenuation for a hydrocarbon release to groundwater are shown schematically in **Figure 1**. Contaminated groundwater is transported from the source at A, through the plume (B), to the receptor at C. MNA is considered successful if the flux and concentration of pollutants is reduced such that the risk to the receptor is acceptably low. Biodegradation of organic contaminants by aerobic respiration, nitrate reduction and sulfate reduction using dissolved electron acceptors (O_2, NO_3^-, SO_4^{2-}) will occur at the periphery or fringe of the plume, driven by mixing between the plume and background groundwater. Slower anaerobic biodegradation by reduction of manganese or iron and methanogenesis will occur inside the plume core, using mineral Mn and Fe oxide fractions in the aquifer sediment, and fermentation processes. Generally, microbial activity and biodegradation processes at the plume fringe are more important for attenuation than processes occurring in the plume core. The plume will grow until the contaminant influx at A is balanced by the rate of destruction of the combined fringe mixing-controlled and the slower internal reactions. Source management measures are typically implemented with NA to reduce the duration and steady-state length of the plume.

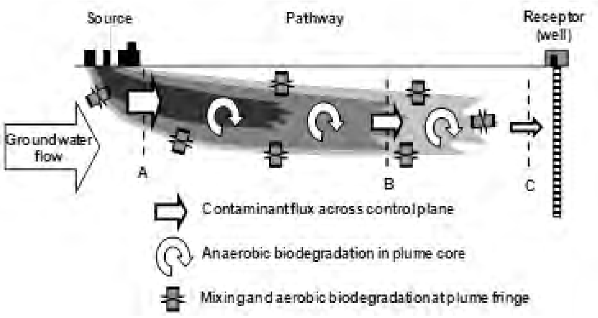

Figure 1. *Conceptual model for natural attenuation of hydrocarbon compounds in groundwater.*

Implementation and performance assessment

Technical guidance is available to support the implementation and performance assessment of NA at sites for different types of contaminants. NA is implemented within the context of the Source-Pathway-Receptor framework (**Figure 1**). This emphasizes detailed characterisation of the contaminant source (supporting plume development) and quantification of NA processes along the plume pathway (aquifer) to predict impacts on receptors. Performance assessment of NA for organic contaminants seeks to (i) characterize the nature and spatial extent of *in situ* biodegradation processes for the contaminants, (ii) estimate biodegradation rates, and (iii) confirm NA occurs at a rate which will reduce environmental risk, protect identified receptors and achieve site management/remediation objectives. It also identifies the need for additional measures if NA will not achieve remediation requirements in isolation. These aims are fulfilled through an intensive long-term monitoring program of groundwater quality and source composition, supported by a technically rigorous evaluation of the site investigation and groundwater quality data. This may involve the integrated analysis of hydrochemical, isotopic, microbiological and other data using a wide range of qualitative and quantitative techniques at different scales to document the occurrence and extent of attenuation. This analysis is formalized within a "lines of evidence" framework, which includes the collection of different types of information:

- Primary line of evidence: Field time-series data showing a consistent reduction in the contaminant concentration or flux over time at one or more points along the source-pathway-receptor linkage, typically used to deduce the status of the plume (i.e. expanding, stable or shrinking), relative to predictions of groundwater flow

- Secondary line of evidence: Field data demonstrating *in situ* biodegradation of contaminants in the plume, typically based on the consumption of dissolved (*e.g.* O_2, NO_3^-, SO_4^{2-}) and mineral phase (*e.g.* MnO_4^-, FeOOH) electron acceptors in the aquifer and a corresponding increase in organic metabolites, inorganic reaction products (*e.g.* Mn^{2+}, Fe^{2+}, HS^-), and other chemical species (*e.g.* dissolved CO_2 and CH_4) that verify different biodegradation processes.

- Tertiary line of evidence: Supporting evidence related to the verification of NA, such as laboratory microcosm studies to quantify biodegradation rates, confirmation of biodegradation mechanisms and pathways using stable isotope analysis, or the use of molecular biological techniques to demonstrate the activity of appropriate microorganisms able to degrade the contaminants

Data analysis and interpretation

Mathematical models are typically used to verify the site conceptual model underpinning the interpretation for NA and to predict the long-term behaviour of the plume for site management. Primary and secondary lines of evidence are obtained from the distribution of dissolved reactants along the plume flow path, using groundwater samples collected from monitoring wells in the plume source area and both uncontaminated and contaminated sections of the aquifer. The plume is presumed to have a centreline, characterized by the monitoring wells, for this analysis. Visual, graphical, and quantitative methods, including regression techniques, statistical analyses, and mass balances are available to interpret these data using concentration versus time and concentration versus distance plots, although flux-based approaches are preferred.

An important objective of this analysis is the estimation of plume-scale contaminant biodegradation rates – often assumed to follow first-order kinetics for mathematical simplicity – to use in numerical reactive transport codes. Similarly, the maximum steady-state plume length and time to plume stabilization must also be predicted, usually to evaluate receptor impacts and remediation timescales. Various mathematical approaches and modelling tools have been developed to undertake this for hydrocarbon and chlorinated solvent plumes, based on different conceptual models of plume development, contaminant mixtures, and biodegradation processes.

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ECG Environmental Briefs **ECGEB No 20**

Light non-aqueous phase liquids: managing site complexities

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Managing risks posed by releases to the subsurface of light non-aqueous phase liquids (LNAPLs) such as petroleum fuels and oils is a complex problem of global concern. Land, groundwater and adjoining surface waters may become contaminated from poor disposal practices or accidental releases during LNAPL chemical handling, storage or transfer. This brief highlights key complexities to consider in the management of LNAPL contamination.

A cornerstone of site management is the development of a conceptual site model (CSM). A CSM integrates the available information and understanding about the site to enable informed site decision making (*1, 2*). Whilst CSMs may often be portrayed as simplified illustrations (**Figure 1**), such images often belie the complexities of the inherent controlling processes and system complexities achieved through site investigation, monitoring, risk assessment and modelling efforts. These are all steered by the growing body of guidance geared to the management of LNAPL contaminated sites (*1-4*).

LNAPL chemical complexity

Although LNAPLs may sometimes comprise a single chemical, releases often involve fuels/oils consisting of complex mixtures of hundreds of hydrocarbons and other additives, such as fuel oxygenates, *e.g.* MTBE (methyl *tert*-butyl ether) (*5*). The overall compound assemblage dictates the bulk properties, such as LNAPL viscosity and density. These influence the migration of the immiscible liquid through the porous or fractured geological subsurface. The low viscosity of petrol enables facile subsurface migration compared to viscous oils or coal tar. Creosote (CTC) products, for example, may require decades for released NAPL to attain a quasi-steady state subsurface distribution. Whilst LNAPLs are defined to be less dense than water and 'float' upon the (ground)water table, densities of CTC products approaching unity cause their inherent chemical composition to control whether they are a LNAPL or a D(dense)NAPL, able to penetrate as an immiscible phase below the water table (*1, 5*).

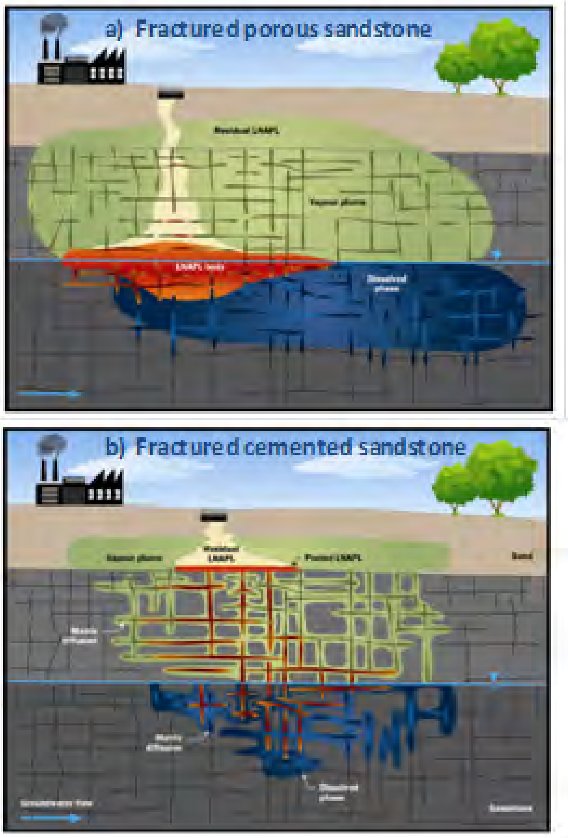

Figure 1. *LNAPL conceptual models (after CL:AIRE, 2014) (1)*

Multiphase flow complexity

Migration of LNAPL represents a complex 'multiphase flow' problem in which LNAPL gas and water phases are present and each are able to migrate within a porous or fractured (fissured) subsurface. LNAPL generally invades more permeable geological horizons and initially migrates downward towards the water table to spread laterally as a buoyant LNAPL (**Figure 1a**). Many factors control the distribution 'architecture' of the LNAPL source zone that develops. Complexities include density, viscosity, composition and wettability, the detailed geological permeability and resident saturation of pore spaces by air and water phases, the mode of release (*e.g.* drip versus catastrophic), and temporal variations of the water table (*2*).

Geological complexity

The geological subsurface is complex. LNAPL migration and fate can differ significantly between various aquifer types, such as chalk, sandstone, limestone, alluvial aquifers and low permeability aquitard units such as clays or mudstones. The latter may offer significant protection for the underlying aquifer (*6*). **Figure 1** contrasts LNAPL fate within a fractured sandstone that is porous compared to one that is cemented, where the LNAPL is unable to directly enter the sandstone matrix. The entry of contaminants is restricted to diffusive transport in the aqueous phase. Example LNAPL conceptual models of a variety of geological systems can be found in CL:AIRE (2014) (*1*).

Chemical partitioning complexity

A subsurface LNAPL source zone can deplete through chemical partitioning. This involves dissolution that continuously generates a migrating dissolved-phase groundwater plume. In addition, LNAPL chemical volatilisation into the soil gas forms vapour plumes that can pose vapour intrusion (VI) risks. These partitioning processes can occur simultaneously and their rates may be significantly influenced by the additional complexity of continual LNAPL redistribution on a (seasonally) fluctuating water table. Individual chemical depletion rates will vary over time, being controlled by both their pure-phase solubility and vapour pressure but also the changing LNAPL mole fraction (Raoult's Law often being used as an approximation (*5*)). Although BTEX (benzene, toluene, ethylbenzene, xylenes) and fuel oxygenates often form key risk drivers with the most soluble/volatile components being preferentially lost, LNAPL mass is often so large that source depletion may still require decades. This is especially so where mass occurs at the interface with, or has diffused into, low permeability units such as clays.

Attenuation process complexity

Many hydrocarbons are prone to biodegradation in the subsurface which can result in the 'natural attenuation' (NA) of migrating dissolved-phase and vapour plumes. Given appropriate conditions, notably sufficient supply of electron acceptors (dissolved oxygen, nitrate, sulfate, etc.) and suitable microbial communities, then biodegradation may occur. Innocuous products and plumes shrink as source zone inputs decline (*1-5*). Whilst biodegradation has hitherto often been assumed to occur on contaminants in the aqueous phase, there is growing evidence from natural source-zone depletion (NSZD) studies that biodegradation may occur within the LNAPL body itself. Moreover, the significance of methanogenesis, gaseous-phase mass loss, and biodegradation in the unsaturated zone mitigating contaminant breakthrough at ground surface have been underappreciated (*7*).

Problem synthesis and management

At the heart of the problem is the continued iteration of the LNAPL CSM. This is central to the management of a specific site scenario. It is obvious that several lines of complexity need to be considered to develop the CSM. It is important to recognise the key roles of site investigation and on-going monitoring of sites in the evolution of the CSM. The quantitative assessments of risks, including analytical/numerical modelling efforts, and the implementation of site remedies to lower risks to acceptable levels and successfully manage and secure progression to site closure are all important (*1-7*, and references therein). A wealth of almost 50 years of experience and research dating from the 1970s is now available to draw upon in our management of LNAPL-contaminated sites.

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Upcoming Meeting

Plastics, From Cradle to Grave and Resurrection

Where: SCI, 14/15 Belgrave Square, London, SW1X 8PS

When: Wednesday 19th June 2019

A conference from SCI's Environment, Health, Safety and Food Group and RSC's Environmental Chemistry, Toxicology and Food Groups.

Synopsis

The use and mis-use of plastics has attracted considerable attention in recent months. The UK government has already pledged to work to reduce waste plastic. The Chancellor, Philip Hammond, announced a £20m fund in the spring budget to help businesses and universities to develop "new technologies" to help achieve the target of eliminating "avoidable plastic waste" by 2042. There will be upcoming funding calls as well as a need to review the whole area to reduce, replace and refine the use of plastics.

This conference brings together key sectors with the aim of focussing on assessing challenges and opportunities for researchers, industry and government. There will be a thematic link between the uses of plastics, their replacement with other materials where it is advantageous, the toxicological hazards and benefits of plastic use and the post-use challenges and opportunities. Abstracts for posters are encouraged, with prizes available for the best poster.

Confirmed Speakers

Peter Maddox, WRAP

Ruth Stringer, Healthcare Without Harm

Margaret Bates, University of Northampton

Peter Reineck, Peter Reineck Associates Ltd

Martin Rose, University of Manchester

John McGeehan, University of Portsmouth

Richard McKinley, Axion

Sally Beken KTN

Registration

https://www.soci.org/Events/Display-Event?EventCode=ENV567

Featured

Things We Don't Know

www.thingwedontknow.com

A science education company that focuses on explaining the questions to which science still seeks answers. It is currently looking for researchers to populate the site with updates on their work.

This website provides a free and easy-to-browse platform that can act as a catalogue of scientific research topics for prospective PhD students, and provides science news with real time updates from scientists working in the field. It also supports reader-directed crowdfunding to encourage popular research topics. *Things We Don't Know* is a C.I.C., or "Community Interest Company", so 70% or more of our profits is used to fund scientific research.

It aims are to reduce graduate dropouts, support the genesis of collaborations, and encourage science and engagement with science.

Sign up to Contribute

Things We Don't Know is keen to sign up more researchers to use the site and provide updates about their work. The website also accepts guest blog posts providing they fit the site's writing guidelines, and will offer editorial support for scientists who want to share what they do.

Video: https://goo.gl/75pzuY

Contact: rowena@thingswedontknow.com

Upcoming Meeting

Latest Advances in the Analysis of Complex Environmental Matrices

Where: The Royal Society of Chemistry, Burlington House, London, W1J 0BA
When: Friday 22nd February 2019

Royal Society of Chemistry Environmental Chemistry Group, Separation Science Group and Water Science Forum Joint Meeting

9.00-9.40 am	Registration and coffee
9.40-9.45 am	Opening and welcome to meeting Dr Roger Reeve RSC ECG UK
9.45-10.15 am	*Mixing high-resolution chemical analysis and machine learning in ecotoxicology for aquatic invertebrates* Dr Leon Barron King's College London, UK
10.15-10.45 am	*Enhanced confidence in river quality monitoring using passive sampling and GCxGC-ToF- MS with tandem ionisation* Dr Laura McGregor SepSolve Analytical Ltd, UK
10.45-11.15 am	Coffee break
11.15-11.45 pm	*Micro- and nanoplastic pollution of freshwater and wastewater treatment systems* Dr Caroline Gauchotte Lindsay University of Glasgow, UK
11.45-12.15 pm	*Exploring the advantages of automated sample preparation and GC-ToF for SVOC and pesticide analysis in environmental waters* Dr John Quick ALS Environmental Ltd, UK
12.15-1.00 pm	Keynote lecture *Environmental cheminformatics to identify unknown chemicals and their effects* Dr Emma Schymanski University of Luxemburg, Luxemburg
1.00-2.15 pm	Lunch break and vendors' exhibition
2.15-3.00 pm	*Temporal and spatial variation in pharmaceutical concentrations in an urban river system* Prof Alistair Boxall University of York, UK
3.00-3.30 pm	*GCxGC-ToF for remote monitoring - Cape Verde Atmospheric Observatory (CVAO)* Dr Katie Read University of York, UK
3.30-4.00 pm	*Liquid chromatography/quadrupole time-of-flight mass spectrometry screening of polar pollutants sequestered by passive sampling devices at the river catchment scale* Prof Gary Fones University of Portsmouth, UK
4.00-4.30 pm	*IC and IC-MS for environmental analysis* Wai-Chi Man Thermo Fisher Scientific, UK
4.30pm	Final questions and meeting close Dr Lee Williams RSC Separation Science Group and University of Sunderland, UK

Delegate Fees

RSC Members £90.00
BMSS/Chromatographic Society Members £90.00 with 19BMC14 discount code
Non-members £120.00
Student RSC members £25.00
Retired/unwaged members £25.00 with 19RU22 discount code
Student non-members £35.00

Registration: www.rsc.org/events/detail/36535/latest-advances-in-the-analysis-of-complex-environmental-matrices

Contacts

Dr Lee Williams, University of Sunderland, 0191 5152215, lee.williams@sunderland.ac.uk
Professor Graham Mills, University of Portsmouth, 02392 84 2115, graham.mills@port.ac.uk
Dr Roger Reeve, RSC Environmental Chemistry Group, 0191 3846907, rgrreeve@gmail.com

Upcoming Meeting

21st Century Chemistry: Disposing of our Nuclear Legacy

Where: The Royal Society of Chemistry, Burlington House, London, W1J 0BA
When: Wednesday 27th March 2019, 12.00 – 5.15pm

This one day Distinguished Guest Lecture and Symposium organised by the Environmental Chemistry Group of the Royal Society of Chemistry explores the intersection of geology, biology and chemistry around radionuclides.

Dr Joanna Renshaw (Strathclyde University)

Dr Renshaw is a microbiologist and radiochemist with extensive research experience in microbial interactions with radionuclides and metals, working at the interface between microbiology, analytical and radiochemistry. She is one of the very few people in the UK who is experienced in both microbiology and the chemistry of transuranic and fission product elements. Her current research focuses on developing novel methods for limiting radionuclide migration in the environment using bacterial biomineralisation processes.

Dr Joanna Renshaw will provide the introduction to the symposium and overview of the subject area.

Professor Mike Wood (University of Salford)

Professor Wood is a research leader in radioecology and Chartered Radiation Protection Professional, delivering consultancy and capacity building within the nuclear sector. A core member of International Atomic Energy Agency working groups on environmental radiation protection, he leads a 5-year research programme in the Chernobyl Exclusion Zone and is a recipient of the Times Higher Education Research Project of the Year award. Other work includes new technologies for ecological research, and managing ecosystem services.

Professor Mike Wood will speak on the environmental impact of our nuclear legacy on the biosphere.

Dr Juliet Long (Environment Agency)

Dr Long is Head of Legacy and Waste Issues in the Radioactive Substances Regulation team at the Environment Agency. An authoritative lead on radioactive substances regulation across UK industries, she promotes big-picture strategic thinking underpinned by technical knowledge, focusing on outcomes and opportunities. She leverages impact for the Environment Agency and the UK, and has delivered significant changes in the strategic direction of government, regulators and industry, driving improved environmental performance.

Dr Juliet Long will speak on the policy of disposing of radioactive waste.

2019 Distinguished Guest Lecturer:

Professor Melissa Denecke (University of Manchester)

Professor Denecke is the Scientific Director of the Dalton Nuclear Institute. She is an international expert in the field of speciation of radioactive material on a molecular scale, with nearly 30 years' experience in X-ray spectroscopy, and in R&D related to the nuclear fuel cycle, notably deep geological disposal of radioactive waste, assessment of contamination legacies and nuclear waste streams separation. Professor Denecke was awarded the Becquerel Medal of the Royal Society of Chemistry for an outstanding contribution to research in radiochemistry. She is experienced in the design, construction, commissioning and operation of advanced X-ray instrumentation for radioactive studies at large scale accelerator facitilites.

Professor Melissa Denecke will present the Distinguished Guest Lecture: *Radiochemistry Research for Safe Nuclear Disposal*.

Registration

To register, visit the RSC event pages and search for "21st Century Chemistry: Disposing of our Nuclear Legacy".

EARLY BIRD before 1st February 2019: £50/£35 for ECG members (free to join as an RSC member)

STANDARD £65/£50