

February 2017

ECG *Bulletin*



Environmental outreach. ECG committee members have been involved in exciting meetings and events aimed at engaging the general public, including the week-long “*Into the blue*” event in Manchester (pp. 8-9) and an interactive event in Oxford exploring possible futures under climate change (pp. 10-11).

Environmental Briefs. We continue our series of short primers on important methods in environmental science with articles on how to assess the indoor

human health risks from volatile organic compounds (pp. 21-22) and on the properties, risks, and remediation of non-aqueous phase liquids (pp. 23-24).

Also in this issue. We revisit the dangers from neonicotinoids for bees (pp. 16-17) and the environmental impacts of rare earth elements (pp. 12-15), announce three exciting upcoming meetings (pp. 18-20), and discuss the implications of changes to the A-level syllabus (pp. 5-6).

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Cover image: A student analyses a bug on a worktable. As Rowena Fletcher-Wood explains on pp. 5-6, upcoming changes to the UK's GCSE and A-level courses in environmental and applied sciences have wide implications for individual students and society. Credit: Comaniciu Dan/Shutterstock

ECG Bulletin

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Chair's report for 2016

News from the ECG

During 2016, your committee arranged a number of successful meetings, events and activities across a range of topics and formats, in some cases jointly with other interest groups, and organisations.

In early March, **Professor Bill Bloss** (University of Birmingham) organised an event on **Atmospheric ozonolysis chemistry**. This two half-day meeting held in Birmingham was attended by fifteen researchers.

This was followed by the **2016 Distinguished Guest Lecture and Symposium** on 22nd March, on the topic of **Geoengineering the climate**. Professor Joanna Haigh (Imperial College) introduced the symposium and spoke on the fundamental scientific ideas behind geoengineering the climate. Professor Michael Stephenson from the British Geological Survey reviewed carbon capture and storage, followed by Dr David Santillo of Greenpeace Research Laboratories, who talked about policy aspects of the geoengineering challenge. The 2016 ECG Distinguished Guest Lecture was delivered by **Professor Alan Robock** (Rutgers University, USA), who spoke on the symposium title. Detailed reports from the meeting may be found in the July 2016 edition of the *ECG Bulletin*. Ninety-six delegates with diverse scientific and environmental interests attended this event.

The ECG has been very active in engaging with younger scientists and early career environmental chemists over the last year. **Rowena Fletcher-Wood** attended the **RSC Early Careers Symposium** in Glasgow in July to showcase outreach volunteering opportunities with the ECG. We also brought together nine volunteers to work on a five-day **NERC Public Outreach** event in Manchester, with a hands-on environmental chemistry stall. The very young visitors to our stall were most fascinated by digging around in our soil trays, seeing dry ice in action, and testing pH. Our early career volunteers are interested in taking part in future events, and our ability to advertise for volunteers has been aided by our social media posts.

Dr Tom Sizmur (University of Reading) resurrected the **early career symposium** format for a successful meeting on the environmental chemistry of water, sediment and soil, which was held at Burlington House on 14th November. A similar symposium is being planned for autumn 2017.

Dr Rowena Fletcher-Wood (Science Oxford) organised a public science talk with audience participation entitled

"Masters of disaster". This event, arranged in conjunction with Science Oxford, was linked to the University of Oxford Environmental Change Institute series of events. The novel format allowed leading scientists to pitch their views on certain topics in a future world, and interactive voting enabled the audience to vote on them.

Alongside our programme of events, ECG Committee members Julia Fahrenkamp-Uppenbrink, Rowena Fletcher-Wood, Tom Sizmur, Rupert Purchase and Roger Reeve continue to produce the biannual **ECG Bulletin**. Professor Martin King (Royal Holloway) is active in developing the **ECG Environmental Briefs**, a series of short reports providing succinct information on all aspects of environmental chemistry. Fifteen ECG Environmental Briefs have been produced to date, including two in this issue, and all are available on the RSC ECG website. We welcome suggestions and potential authors for future Environmental Briefs.

To date, the ECG has arranged three meetings which will take place in 2017 at Burlington House, Piccadilly: the 2017 ECG Distinguished Guest Lecture and Symposium **"Inside the engine: from chemistry to human health"** on 1 March 2017; a meeting entitled **"What's new in the analysis of complex environmental matrices?"**, organised jointly by the ECG, Separation Science group, and Water Science Forum, to be held on 3 March; and a meeting on **"Emerging contaminants in waters and soils: public health concerns"**, which is being organised in conjunction with the RSC's Toxicology Group and Water Science Forum, on 5 April.

ECG membership has grown to just under 1900 members. We are aiming to recruit more committee members in 2017. Anyone wishing to help with editing the *ECG Bulletin* is particularly welcome as we are looking for a new editor this year. We would also like to put more effort into our social media outlets, a new ECG website, and digitising and cataloguing some of the *ECG Newsletter* and *ECG Bulletin* archive (1995–2017).

The committee is always keen to hear from members, including feedback on events, suggestions for future activities, and other ideas, and we look forward to seeing you in 2017. I would like to thank the committee and those who have participated in the diverse activities of ECG for their enthusiasm and for volunteering their time.

Zoë Fleming
NCAS, University of Leicester

The ECG Interview: Martin King

ECG committee member Martin King is Professor of Atmospheric and Cryospheric Chemistry in the Earth Sciences Department, Royal Holloway, University of London.

What inspired you to become a scientist?

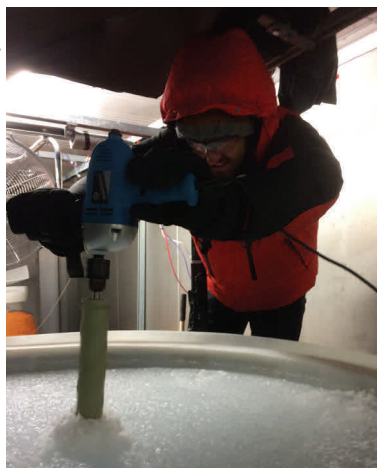
During my A-levels studies, I attended a talk at the Cavendish Physics Laboratory in Cambridge by Joe Farnham about ozone hole chemistry. I was the youngest there by at least ten years and what felt like thirty years. The talk was a bit dry for a seventeen year old. But three truths suddenly came clear to me: a few simple chemical reactions could have an enormous effect on the planet, science could be my ticket to some interesting places in the world – including Antarctica – and chemistry was not all about making new compounds, but could be used to explain the natural world.

How did you come to specialise in atmospheric and cryospheric chemistry?

I wanted to go to Antarctica. My 4th year degree supervisor Professor Richard Wayne studied atmospheric chemistry and ozone. I wondered if this was my ticket, and it was: by applying my love of physical chemistry to the real world. I enjoyed my 4th year research so much that I stayed on to complete a DPhil in Atmospheric/Physical Chemistry, and gave up my other desire to be a fast jet pilot. I carried out post-doctoral work in Fairbanks, Alaska, where I was introduced to the chemistry of snow and ice. I later took up an appointment in London, and subsequently worked in Antarctica with Italian scientists in Terra Nova Bay.

Could you describe your current job?

I could say that I am a Professor of Atmospheric and Cryospheric Chemistry in the Earth Sciences Department, Royal Holloway, University of London, but that does not help describe what I do. A better question might be: what did you do last week? And I would say that on **Monday**, I fixed the leak on a two-tonne sea ice tank used for measuring the effect of volcanic ash on planetary albedo. On **Tuesday**, I was an examiner for a PhD viva (the student passed with flying colours). On **Wednesday**, I met



with three PhDs students to explore the spectroscopy of ice-bound nitrate, derived the error equation for an optical tweezers experiment, and found a bug in a radiative-transfer programme. I also taught crystal structures of simple silica minerals to first year students and attended a faculty teaching meeting. On **Thursday**, I completed risk assessments for reacting ozone with organic chemicals from tree leaves to make atmospheric aerosol, worked on a grant application, and attended a plagiarism meeting. On **Friday**, I taught statistics to third year

students and then drove to the Rutherford-Appleton neutron facility to spend three days and nights of the weekend bouncing neutrons off an oily film one molecule thick found at the air-water interface between cloud water and the atmosphere.

What is your advice for anyone considering a career in this area?

The advice I give regularly to students is to not specialise in the environmental aspects too quickly. In my opinion, it is much better to undertake a physics, chemistry, biology or engineering degree and then specialise in environmental aspects later. Whilst this is the route I have taken, and so of course I think it is the best one, I find that nearly every day I am using skills from my core subject applied successfully to environmental problems.

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

There is a lack of diversity in topics studied, and too much pressure for groups and teams to conform with common ideas. In my opinion, this leads to a lack of diversity of ideas and too much effort spent on one topic, when there are so many other interesting problems that need studying.

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

Working with PhD students.

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

I still think I would have made a great fast jet pilot.

Article

In the bin – Applied and environmental sciences at school

Rowena Fletcher-Wood (Science Oxford)

In yet another recent Ofqual overhaul of GCSE and A level examinations, changes have been made to the way in which school science labs are run and assessed, and subjects including environmental science and applied science A levels are under threat of being scrapped from 2017.

Interdisciplinary collaboration is a rising trend in scientific research, from bioinformatics to enzyme-directed chemical synthesis to geoengineering or planetary astronomy – and for good reason: it is effective. By confining ourselves to narrow fields and declining to engage in research that transgresses the boundaries of our disciplines, we miss out on everything that cannot be understood in terms of single disciplines, which is most things. Researchers are more and more aware of this – and yet at the same time, in schools we are heading back to traditional subjects.

The loss of so-called “soft” subjects such as environmental science has provoked criticism [<https://www.theguardian.com/education/2015/mar/03/ofqual-provokes-government-scrap-science-practicals>], suggesting that less academic students will be underserved, unable to obtain the required grades in the traditional science subjects (physics, chemistry and biology) that will allow them access to scientific or related fields such as nursing or conservation. However, Ofqual claims that their decision to eliminate them has nothing to do with these subjects being “soft”, but arises from difficulties with standardising exams. As only a few thousand students sit these applied A levels, the demand is not considered sufficient to warrant keeping them.

Environmental Science

This subject covers such topics as energy resources, sustainability and the environmental impacts on health. It overlaps overtly with biological, geological, geographical, atmospheric, physical, and chemical topics, whilst entwining the scientific information into its political, sociological and economic context. And the



***Studying science.** Upcoming changes to the UK's GCSE and A-level courses in scientific subjects have wide implications for individual students and society.
Credit: Comaniciu Dan/Shutterstock*

importance of this should be heavily underlined, as the contextual placement of science is often overlooked by the traditional subjects, where the story of progress is one of uncovering something absolute that was always there waiting.

Instead, I believe the decision-making complications integral to industries such as nuclear energy should be introduced in parallel, if nothing else so that the scientists can sympathise with public concerns (as many don't) and the policymakers responding to them are scientifically literate (which few are). Also important in the course are the research and investigative skills that allow students to develop an understanding of the demands in data and measurement rigour and how to appropriately weigh and assess scientific evidence. And naturally, the topic of environmental science demands being up to date with recent advances, meaning that the course's factual content is more frequently revised and the quality standard is high.

Applied Science

This subject, which I am currently teaching, focuses on independent research conducted by the students, the legal and practical delivery of health and safety at work,

case studies into medical, environmental, educational, industrial and service science, and hands-on laboratory work. Although the course is sparingly explained in the specification, with no example case studies and huge flexibility, it is designed to allow the deliverer to cater for the interests of the students who are taking it, both as a group and individually, working to a standardised level to explore anything from paint manufacture to radiology, and developing skills that one would normally be trained in whilst working or doing postgraduate research. These may be soft skills, but they are essential ones, and ones that do not come first in the academic route but either later (during postgraduate study), or sometimes not at all. Whilst the scientific knowledge acquired is unpredictable and can therefore only be tested via coursework, the course does include hard scientific knowledge and a mathematical requirement. Instead of testing facts, the exams focus on critical and creative problem-solving using taught scientific techniques, methodology and rigour, engaging in principles rather than crammed facts.

the applied science course opens the door to a perspective of science ... that is resourceful and imaginative, like a hard crossword puzzle that sucks you in and makes you determined to finish it.

In my opinion, the applied science course opens the door to a perspective of science different from the true/false black/white image that puts off many children who would make valuable scientists. Instead it is resourceful and imaginative, like a hard crossword puzzle that sucks you in and makes you determined to finish it. I would argue that by eliminating applied subjects we are not merely underserving the less academic students, but everybody, reducing the gain in applied skills that are, in the real world, as valuable as academic ones. In fact, we are underserving them already, because students capable of taking the traditional subjects are steered away from considering applied ones on the understanding that they will lower their trading value by stooping to soft subjects. In school, I would never have taken an applied lesson, and yet I would have loved the independent learning and practical dimensions and thrived under it. And if I'd never taught, I would never have read the courses and reconsidered the hard/soft subject story.

Wider implications

There are other ways I think in which these changes underserve – and that is socioeconomically. Now that all students have to do A levels, by limiting the breadth of sciences and science skills we are in danger of creating a bottle-neck. Subjects like physics, chemistry and biology prepare students to go to university and study physics, chemistry, biology (or medicine or biochemistry), but

not to get jobs. These students are still missing most job skills. So they have to go to university. And those who do less well in traditional subjects and get lower grades won't get university places or won't embrace the experience; they will be stuck, in a climate with mass unemployment and not enough apprenticeships, with a bunch of A levels, no working skills and no experience.

The traditional way to get out of this scenario is to do volunteer work, but this creates another socioeconomic problem – class divide. Whilst the well off can afford to do endless internships for free whilst paying for their own food and travel to gain invaluable industry experience, many can't, especially when faced with pressures such as family illness or children of their own (and the less well off and less well qualified tend to have babies younger). This can only have one consequence: the diminution of the worth of the degree, and a one-route-to-any-career mentality, forcing people to go back and retrain or buy back into the old-fashioned career-for-life prospect.

Although some exam boards are planning to overhaul the environmental science course in the hopes of saving it from the ruthless sword of Ofqual, it remains under threat, whilst applied science is almost certainly doomed. New changes to laboratory sessions also mean that there are no practical exams, only a lab quota that teachers must sign off. Crucially, this means that poorer schools with fewer resources can (and will) do fewer labs, redistributing their budgets to save on science practicals and so produce students with less experience and less complete understanding than their privately schooled peers – and this, in my opinion, is the kind of consolidating understanding that makes all the difference in university interviews and bridging the school-university leap.

This is well summarised by the Wellcome Trust, who, after consultation with Ofqual on their proposals for the discontinuation of some subjects, asked, "Who chooses to study them?" (Ofqual: GCSE reform consultation Response by the Wellcome Trust August 2013; <https://wellcome.ac.uk/sites/default/files/wtp055604.pdf>).

By reducing access to environmental and applied science courses or abolishing them, we thus risk exacerbating social divisions, as well as reducing the life chances of students who are less well off.

Meeting report

Early careers researchers meeting on the environmental chemistry of water, sediment and soil

Steve Leharne (University of Greenwich) and Tom Sizmur (University of Reading)

Twenty-nine delegates attended this ECG event on 14 November at Burlington House. The aim was to provide a supportive environment for doctoral and postdoctoral researchers and early career scientists in industry to present recent research findings, network with fellow early career researchers, and hear about the career opportunities available to professional environmental chemists. Eight oral and eleven poster presentations were made by early career researchers.

The meeting started with a presentation from Katerina Kademoglou (Reading University) on a novel analytical method, which used a dialysis membrane containing Tenax to measure the bioaccessibility of flame retardants in indoor dust. Helen Balshaw (Swansea University) then described the possible use of pyrene – a fluorescent probe – to examine the polarity and viscosity of the organic environment in water repellent soils, and Abdolbaset Karim (University of Nottingham) reported on an investigation of ^{129}I bioavailability in vegetables grown in soils taken from Northern Iraq.

A coffee break provided an opportunity for delegates to view and discuss the posters, whose contents ranged from soil micronutrient deficiency to organic pollutant uptake by plants, and the fate of plasticisers and pharmaceuticals in the environment. A poster by Saeed Ahmad (University of Nottingham) on the geochemistry of iodine and selenium in North East Pakistan was judged to be the best poster on display.

The meeting proceeded with former ECG committee member Dr Cecilia McLeod (Director Geo-Environment, WYG Global Consulting) describing her work as an environmental chemist in ameliorating a toxic waste



Saeed Ahmad receives his prize for the best poster presentation.

dump generated by Irish Steel on Haulbowline Island in Cork Harbour, Ireland.

The first afternoon session heard presentations on evaluating landfills for their resource potential (Steven Warwick, Cardiff University); examining the effects of physicochemical parameters on the bioavailability of metals and hydrocarbons in soil mesocosms (Sabrina Cipullo, Cranfield University); and on the coupling of phyto- and myco-remediation on petroleum contaminated soils in the Niger Delta, Nigeria (Udeme Dickson, Nottingham Trent University). The final session commenced with a presentation by Heather Sanders (Nottingham University) on the interactions of ^{129}I and ^{77}Se with humic acids, followed by Alun James' (Aberystwyth University) account of the use of biochar derived from reeds to treat minewater in an upland environment. Alun's presentation was judged to be the best oral presentation of the meeting.

The meeting concluded with Professor Chris Collins (Reading University) recalling his life as an environmental chemist in an academic environment. In particular, he emphasised his interests in the uptake of organic chemicals by plants; the fate and transport of pollutants in soils; and the use of a human gut simulator to measure the bioavailability of soil contaminants.

Outreach

Environmental chemistry team at the NERC “*Into the blue*” public event

Zoë Fleming (University of Leicester)

A team of ten young scientists helped out at the NERC “*Into the blue*” environmental science showcase event in Manchester during half-term in October 2016. These are our experiences of the five days of demonstrations and talking to the public, and our motivations for sharing our enthusiasm for the subject with parents and children.

The Natural Environment Research Council (NERC) organised a large outreach event this year. This followed the success of allowing visitors on board the NERC’s *Discovery* research vessel last year, whilst it was anchored in the Thames in London. This year, members of the public were allowed to inspect the NERC’s dedicated aeroplane for atmospheric and oceanic research at Manchester airport. In an adjacent hangar, a host of environmental science outreach activities and stalls were on display. The whole event attracted much media interest (BBC Newsround, Sky News and BBC evening and regional news programmes). Just over five thousand members of the public visited over five days, and two hundred stakeholders and VIPs attended the evening events.

Each of the five NERC research centres had been encouraged to come up with an idea for a stall for the

exhibition. Our team decided on a general environmental chemistry theme, which included some of the successful activities we had used for previous RSC-sponsored outreach activities:

- 1) Ocean acidification (adding dry ice to an alkaline solution and seeing the indicator change the pH to acid).
- 2) Soil testing (picking out microplastics in the soil and investigating them with a smart phone microscope and then testing the soil for pH, nitrates and phosphates).
- 3) Introducing zeolites to extract Fe- or Co-contaminated solutions.
- 4) Atmospheric chemistry (small sensors measuring air pollution).

The volunteers were recruited through ECG social media plus friends and colleagues, and ranged from teachers, science communicators, environmental consultants, an undergraduate, a PhD student, an early career RSC committee member, and post-doctoral researchers. The RSC NW region education officer, Charlotte Still, also joined in. We all shared a flat locally, so enjoyed the rare downtime we had at the end of the long days. We will keep in touch for future outreach opportunities as the team worked well together, and each individual brought their own perspective to the demonstrations.

Volunteers’ impressions Callum Taylor

I am currently on my placement year of my degree in Forensic and Analytical Science at the University of



Rowena Fletcher Wood, Zoë Fleming, Beth Dowler, Matthew Savage and Marios Panagi were among the volunteers who helped at the stall.



Eloise de Spretter, Nikita Bhalla and Callum Taylor also volunteered. Two other volunteers, Alice Ughi and Charlotte Still, are not in the photos.

Huddersfield. I have been a member of the RSC for over a year now, and I jumped at this opportunity to volunteer for a few days.

In some areas of science, keeping the public involved and updated with developments in specialised research is perhaps not too important. However, in the environmental sciences, it is crucial because everyone, from a child in primary school to the CEO of a FTSE 100 company, contributes to the environmental challenges faced by society. Outreach events such as “*Into the blue*” stimulate interest and awareness among the public and even among other scientists about this topic. This event opened my eyes to the scale of environmental research in the UK, particularly the monitoring programmes in oceanic and atmospheric research. I also found the British Antarctic Survey stall very stimulating.

Volunteering for the ECG at this event has shown me the variety of career paths available to the younger scientist. For example, monitoring pollution or finding innovative solutions to handling disposal. I learnt that communicating your scientific discoveries to the public can be difficult due to varying levels of education and interest. To engage younger generations with science and the environment with demonstrations and fun hands

I too jumped at this chance to help with the Environmental Chemistry Group’s stand at the “*Into the blue*” event. It was an exciting opportunity to talk to the public about something I care about, and to meet those conducting research in the environmental sciences. Communicating science to the public is extremely important and also challenging. This is particularly true of environmental science, which incorporates so many different concepts. “*Into the blue*” succeeded in communicating these ideas to the public, through fun, games and hands-on exhibits. At the ECG stand, I found children were excited to dig in the soil to see what they could find and were asking, “How did plastic get there?” Parents asked what they personally could do to help make a difference and reduce the amount of plastics that end up in our oceans. Many people commented that the event had opened their eyes to a whole world of environmental challenges that they had not considered before.

It wasn’t just visitors who had the chance to see the research presented at this event; I had an amazing time meeting and speaking to the other exhibitors. I particularly enjoyed the tour of the NERC research aeroplane and visiting the British Antarctic Survey stall, where you could see the amount of preparation, work,



Callum demonstrates the ocean acidification demo.



Eloise helps children to test soil for pollution.

on experiments, such as our dry ice experiment, will surely spark interest for some of them to continue with science later in life. In terms of my own career, this event has shown me that there are many paths available, and so being bound to a rigid plan for the future is not necessarily more beneficial than a flexible one. To adapt John Donne, it is no one person’s duty to look after the earth, it is all of ours.

Eloise de Spretter

I graduated in July with integrated Masters Degree in Environmental Science, and am now working in the agriculture sector as a scientific data administrator.

time and effort that takes place before an expedition. Sometimes studying the environment can feel all doom and gloom. However, this event has inspired me and I believe it inspired many of the visitors too.

Further information

NERC research aircraft in Manchester in the News: http://www.bbc.co.uk/news/video_and_audio/headlines/37770945

NERC’s “*Into the blue*” website: <http://intotheblue.nerc.ac.uk/manchester/>

Meeting report

Masters of disaster – click to change the world

Rowena Fletcher-Wood (Science Oxford)

This interactive, public event was hosted by Science Oxford and the ECG. It took place in Lady Margaret Hall, Oxford, on Monday 21 November 2016 and was attended by thirty-two participants. The event diverged from other events by making use of interactive technology and by encouraging academic speakers to speculate about the future based on their expert knowledge. The audience was able to steer the direction of the debate and explore possible futures.

Imagine yourself a hundred years in the future. No further changes have been made to mitigate climate change and we are now in an energy crisis, places like Oxford are flooded continuously, and food scarcity is a global problem. What can we do to address and prioritise these issues? At the start of the event, each speaker gave a 5-10 minute talk or “pitch,” followed by an audience vote using Turning Point handsets – an interactive technology that allows live vote collection and data display in Powerpoint presentations. Following the revelation of the votes, the speakers responded, and the story of the future’s crisis unfolded.

Speaking at the event were Dr Caspar Hewett (Newcastle University), Professor Myles Allen (University of Oxford Environmental Change Institute), and Dr Marcus Springman (Oxford Martin School). The event was chaired by Dr Michaela Livingstone from Oxford Sparks, a public engagement platform for science at the University of Oxford.

Dr Caspar Hewett first put forward the case for both large- and small-scale flood interventions, from draining reservoirs before predicted heavy rainfall and digging

holes to divert excess water and delay its entry into rivers, to planetary-scale geoengineering approaches. The two geoengineering methods that he supported were the use of “Salter’s ships” spraying seawater into the air to increase Earth’s albedo, thereby reflecting the sun’s rays back into space and cooling the planet, and CO₂ sequestration using artificial trees (*for more information on geoengineering see the July 2016 edition of the Bulletin, which reports on the Distinguished Guest Lecture on this topic held in March 2016*). The benefit of these technologies, Dr Hewett argued, was that they (unlike other proposed geoengineering methods) could be turned off at any time, were we to realise that their negative effects outweigh their positive ones.

Professor Myles Allen took a rather unusual stance on energy, arguing that the public should not foot the bill or make the effort to save energy. Instead, we should create pressure and convince government to make energy companies responsible for mitigating the CO₂ they put out into the environment – not by paying a carbon tax, but by mitigating all of it. This mitigation could be done by planting artificial or real trees, or through underground carbon storage in natural rock cavities. On the

Professor Allen declared the energy problem virtually fixed, with no more net CO₂ emissions and with clean-up underway via the already proposed artificial trees.

other hand, Professor Allen argued against the introduction of geoengineering via albedo changes: “It’ll never catch on”, he declared, outlining the problems associated with switching it off again, as well as conflicts over governance and the varying effects that it would produce across the world.

Dr Springman’s arguments for a food-based focus initially also centered on climate change mitigation. The speaker argued for a reduction in methane emissions, which contribute around a quarter of the greenhouse gas effect because methane is a much more potent greenhouse gas than carbon dioxide. He proposed several solutions for this, beginning by cutting red meat consumption by 10% to see a fall in methane emissions by 20 to 30% and a concomitant improvement in public health.

In the initial audience vote that followed these pitches, the proposed energy measures obtained the most votes, with food interventions a close second and flooding interventions trailing behind (**Figure 1**). Professor Allen declared the energy problem virtually fixed, with no more net CO₂ emissions and with clean-up underway via the already proposed artificial trees. Dr Hewett bemoaned the widespread disasters that would result from neglecting flooding, causing him to propose his same measures again.

Following the first vote, Dr Springman focussed more on the human health element of meat consumption and argued for taxing foodstuffs according to their health impacts and methane content. Such a tax would heavily incentivise micronutrient-rich diets, with significantly lower meat and dairy consumption, escalating the price of a burger to around £30. This suggestion, however, was not popular. The second round of voting saw a swing in the opposite direction, with overwhelming support for flooding interventions.

However, the vote rapidly yo-yoed again after governance issues in geoengineering were explored in more depth, “Meat free Mondays” were introduced and Dr Springman went on to propose improving sustainable eating education to caterers, especially in schools, including choosing food with health benefits and lower carbon footprints. The audience were quite taken with this softer approach in the third round of voting; however, Dr Springman argued during questions that education actually has a negligible impact given the resources that go into it, and that taxation, however much we may like burgers and dislike taxing their consumption, is actually much more effective.

Professor Allen ended by proposing a rescue mission for Greenland. He argued that, given delays in geoengineering and carbon cleanup according to the vote, the ice may now be melting at a critical rate, risking sea level rises of up to 20 meters, causing huge losses of land worldwide well beyond the localised flooding we heard about earlier, changing sea temperatures and devastating ecosystems.

Ending on “a silly note”, Dr Hewett proposed meeting flooding issues halfway, abandoning cities that had been affected and developing new island colonies that employed Venetian-style ocean transport. The final vote saw 46% for “water world adaptations” and 32% to save Greenland (**Figure 1**).

Whilst the voting patterns appear indecisive, they might also indicate that all issues were similarly important. But this was not the last vote: no event would be complete without evaluation data, and the handsets came in handy

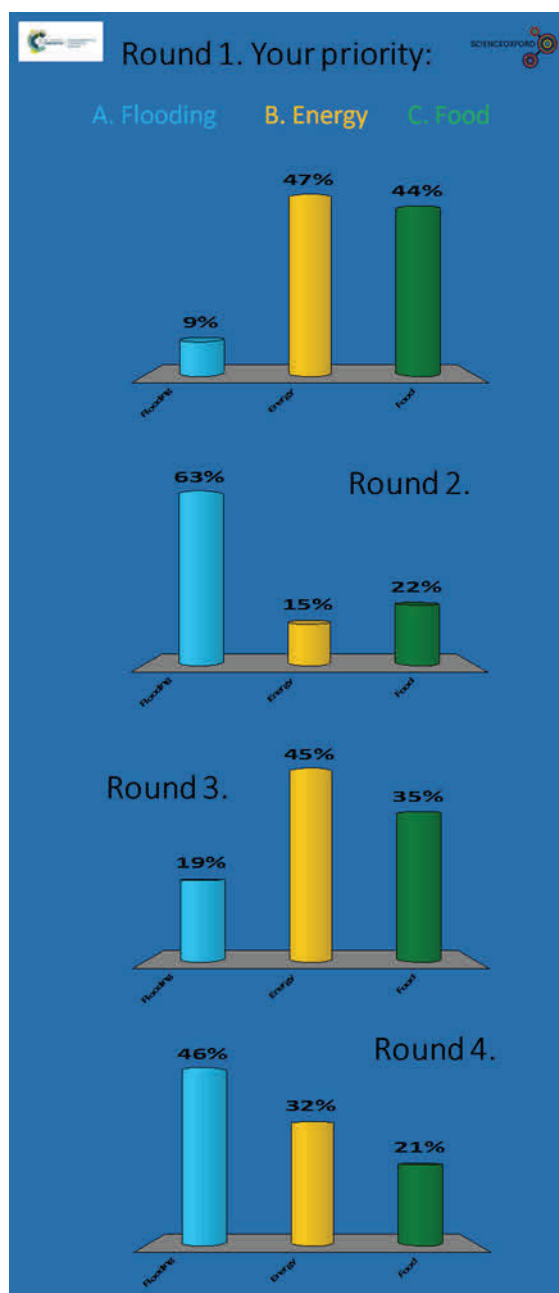


Figure 1. Votes from the four rounds.

for collecting information. 44% of the audience voted the event excellent, and 25% admitted they had never been to a science event before. Attendees were mostly local, with 87% coming from Oxford/Oxfordshire, 10% from further afield, and 3% from abroad, most having connected to the event through Oxford University or Science Oxford.

Science Oxford runs a year round programme of events for adults and families, which can be explored at scienceoxford.com/events.

Article

Rare earth elements: Chemistry, fate and environmental impact

Tom Sizmur (University of Reading)

The use of rare earth elements (REEs) in industrial, medical and consumer products is increasing rapidly. REEs are important components of the new technologies such as wind turbines and electric vehicles, that are vital to the transition to a low carbon economy. Because of their chemistry and speciation, REEs are rarely present in a form that can cause toxicity, but REE concentrations are noticeably elevated in surface waters and sediments globally. This article explores the current and future uses of REEs and discusses the possible environmental impacts of REE emissions.

REEs, also known as the lanthanide elements, are a group of 15 elements with atomic numbers 57 to 71 (**Figure 1**). Despite their name, they are not particularly rare. For example, Ce (the most abundant REE) is more abundant than Cu or Pb and several REEs are more common than Sn, Mn, Ag or Hg. The REEs often occur together because they are chemically similar (all have an oxidation state of 3+, have similar ionic radii and all inhabit the same row in the periodic table), which enables them to substitute for each other in crystals. There is, however, a small but consistent decrease in ionic radius with increasing atomic number which occurs alongside a decrease in abundance. REEs with atomic numbers 57 to 63 are considered light REEs (LREEs) while those with atomic numbers 64 to 71 are considered heavy REEs (HREEs). The REEs with an even

atomic number are more abundant than REEs with an odd atomic, according to the Oddo-Harkins rule that describes proton pairing during star formation.

Pure forms of REEs tend not to exist in the environment because they are very reactive and form part of the crystalline lattices of minerals. Even after weathering, they are usually incorporated into secondary minerals and remain immobilised. Many REEs were originally isolated in the 18th and 19th century, but only efficiently in the 20th century. Apart from Ce, La, and Nd, REEs were not commercially available until 1940s. The market for REEs has arisen in the last fifty years, and demand is expected to increase exponentially in the next twenty-five years. Up until 1985, most REEs originated from minerals mined at Mountain Pass in California. However, China emerged as a major producer in the 1990s with extraction of REEs from ores located at the Bayan Obo Iron deposit, Inner Mongolia. As a result, China now supplies more than 90% of the global output of REEs.

The properties of REEs are exploited to produce a wide range of consumer products. REEs have been used in China in fertilisers and as feed additives for livestock. There is some evidence linking this application to increased crop yields, and to gains in animal body weight and enhanced milk/egg production (2). REEs are incorporated into catalysts for petroleum cracking in oil refineries. Cerium carbonate and cerium oxide are used in diesel fuel additives and in catalytic converters, resulting in the release of CeO₂ nanoparticles in vehicle exhausts. Phosphors for fluorescent lighting contain several REEs (Tb, Ce, and La for green and blue emissions, and Eu for red emission). However, the environmental impact of REEs in these phosphors is often overlooked because they also contain Hg, used to produce natural white light. Some MRI contrast agents, e.g. gadopentetic acid, contain Gd as a complex ion. Oral

LANTHANIDES	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.5	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
	89 Ac Actinium 227	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

Figure 1. The lanthanides and actinoids are referred to as rare earth elements.

or intravenous administration of the contrast agent results in urinary excretion of the absorbed Gd, where it enters wastewater treatment plants (see below). Several applications of REEs are a direct result of legislation to improve air quality (e.g. Ce in catalytic converters) or the transition to a low carbon economy. For example, Nd, Dy and Sm are used in the manufacture of magnetic alloys for hybrid engines and in permanent magnets for wind turbines (as well as a whole host of consumer electric goods such as headphones, computer hard drives, and electric motors). Nickel-metal hydride rechargeable batteries for electric and hybrid vehicles may contain La Ce, Nd, or Pr as the anode.

Environmental fate

There are very few studies of the environmental fate of REEs. Because they are considered less toxic than many other elements (e.g. As, Cd, Cr, Hg, Pb), the environmental impact of REEs is often overshadowed by these other elements. For example, when REE ore is mined, the major hazards are associated with other toxic metals present in the REE-bearing ore and in waste streams. Waste materials from REE processing are naturally radioactive due to the presence of, for example, thorium and uranium radioisotopes. Clean-up costs for spillages of radioactive wastewater from the processing of REE ore at the Mountain Pass mine in California contributed to its decline and closure in the 1990s. Despite these hazards, REE mining is generally considered to have a low environmental impact. REEs tend to be present in carbonate minerals rather than in sulphides, meaning that acid mine drainage is less common at REE mines than other metalliferous mines.

The impact on the environment from the use of REEs was first detected in the early 1980s. Analysis of sediment cores collected from the San Pedro Shelf, just south of Los Angeles in California, revealed 890–6900 times more light REEs (La, Ce, Nd and Sm) than present in crustal material (3). The REEs were traced to a wastewater outfall discharging into the basin that served 3.5 million people, tens of thousands of businesses and industries, and, importantly, seventeen oil refineries. Most wastewater is discharged into rivers where REE contaminants may be deposited on land during flood events or carried out to sea. About 1.5 tonnes of anthropogenic La is discharged into the North Sea from the river Rhine every year. The source of this

contamination is an industrial plant near the city of Worms in Rhineland-Palatinate, which uses fluid catalytic cracking agents. La concentrations (49 ppm) in the plant effluent exceed levels known to cause ecotoxicological effects (4).

Gadolinium from MRI contrast agents is the most ubiquitous REE discharged into rivers via wastewater treatment plants. The relatively stable Gd complex is soluble in aquatic ecosystems. As a result, influent and effluent of wastewater treatment plants is often enriched in Gd, but an elevated Gd concentration is not found in sewage sludge. Nozaki *et al.* (5) found evidence for elevated Gd concentrations in three rivers, which discharged into Tokyo Bay. They concluded that not only population size, but also the degree of modernisation of medical treatments affects REE enrichment in the environment. It has been suggested that, due to its solubility and ubiquity, Gd could be used as a tracer of other emerging contaminants discharged from wastewater treatment plants, which are more difficult to analyse, such as pharmaceuticals or personal care products (6).

In an ecological risk assessment of REEs on aquatic organisms in rivers, ecotoxicity tests were performed for several aquatic invertebrates. From the dose-response curves, Predicted No Effect Concentrations (PNECs) were computed for Ce, Gd and Lu. These PNECs were used to produce risk quotients by comparison with a global dataset of REE concentrations in rivers (7). Risk quotients were above 1 for some locations (e.g. effluent from a wastewater treatment plant downstream of a hospital or residential area), indicating that REEs were present at concentrations above their PNECs.

Toxicity

Because REEs are chemically similar, one might expect their ecotoxicological effects also to be similar. However, a current lack of knowledge on the mechanisms of toxicity of REEs precludes this assumption. Most ecotoxicology studies have focused on freshwater organisms, and there are only a few published salt water or terrestrial studies (8). Toxicity seems to decrease with increasing atomic number due to higher stability constants of the heavier REEs, indicating that the speciation of the element is of greater importance than its chemical identity. The influence of speciation (and thus bioavailability) on toxicity is paramount as the REEs

Toxicity seems to decrease with increasing atomic number due to higher stability constants of the heavier REEs, indicating that the speciation of the element is of greater importance than its chemical identity.

are usually present in the 3+ oxidation state so they can form soluble complexes with nitrates, chlorides, and sulphates. In highly complexing media, REEs form insoluble species with carbonates, phosphates and hydroxides, which means their toxicity could be underestimated in these solutions. REE complexes become less soluble with decreasing temperature and increasing pH or redox potential. Thus, chemical speciation modelling is required to estimate the free ion concentration in solutions and to predict toxicity.

Most toxicological data relate to Ce and La, with a little information on Gd and Nd, but virtually nothing for the other REEs. REEs have a similar ionic radius to calcium and so can replace Ca in cell functions or block Ca channels. However, the most widely reported mechanism of toxicity is a redox imbalance in cells that leads to oxidative stress. Several studies have used reactive oxygen species (ROS) or antioxidant activities (superoxide dismutase, catalase, and glutathione peroxidase) as a toxic endpoint (9). There are reports that REEs have a beneficial effect at low concentrations and adverse effects at higher concentrations (hormesis). For example, the stimulation of antioxidant enzymes in plants with low La levels could be interpreted as a toxic response, but the effect has been found to be positive at low concentrations, helping the plant to defend against ROS caused by other stresses (8). This mechanism may be responsible for the increased crop yield and livestock growth rates observed in response to REE additions to fertilisers and feed additives in China (2).

Relatively little attention has been paid to the effects of REE exposure on human health. Studies have primarily focused on monitoring populations who reside next to REE mines in China. An investigation of residents living close to the Bayan Obo Iron deposit in Inner Mongolia found REE levels in hair samples above those from a control area (10). Concentrations were higher in male hair than female, and higher in miners than non-miners, indicating occupational exposure. Accumulation of the light REEs also increased with age, which suggests a slow excretion rate and the potential for bioaccumulation. A similar study conducted in a large-scale mining area located in Hetian Town of Changting County, Fujian Province, Southeast China showed that REEs from mining were present in the soil, water and vegetables produced in the vicinity of the mine, and these were associated with elevated concentrations in the hair and

blood of local farmers (11). A risk assessment indicated that the ingestion of contaminated vegetables did not exceed values known to be hazardous for human health, but that long term exposure should be considered.

Recycling and recovery

China produces more than 90% of the global REE output and imposes a quota on the export of REEs. This restriction is encouraging the recovery and reuse of REEs. Less than 1% of REEs in 'end-of-life' products were recycled in 2011, but there is considerable scope for recycling the REEs used in permanent magnets, lamp phosphors, rechargeable batteries and catalysts (12). Because REEs usually occur together in a fixed ratio, some may be stockpiled while there is a high demand for others, and thus their demand is controlled by the element in most scarce supply. For example, because Nd is much less common than La or Ce, mining ore for Nd produces an over-supply of La and Ce. Future demand for electric vehicles and wind turbines will rely heavily on Dy and Nd, which are used in permanent magnets. Because these technologies are important components of our strategy to transition to a low carbon economy, the supply of REEs has been highlighted as critical to achieving carbon neutrality. It has been predicted that the supply of Dy and Nd will need to increase by 700% and 2600%,

Less than 1% of REEs in 'end-of-life' products were recycled in 2011, but there is considerable scope for recycling the REEs used in permanent magnets, lamp phosphors, rechargeable batteries and catalysts

respectively, between 2010 and 2035 if atmospheric CO₂ is to be stabilised at 450 ppm using current technologies (13). The REEs of greatest concern are therefore those that are of high importance to clean energy and also have a high supply risk (Nd, Dy, Eu and Tb). One of the best opportunities for recycling is permanent magnets which are based upon neodymium-iron-boron (NdFeB) alloys and also contain Dy, Pr, Gd and Tb, representing some of the most critical REEs in terms of future supply risk. There are also opportunities for recycling REEs from nickel metal-hydride batteries and lamp phosphors.

Several studies have sought to identify the opportunities for recovering REEs from mixed waste streams. Commercially recoverable quantities of REEs, primarily Ce, have been detected in landfills by Gutiérrez-Gutiérrez *et al.* (14), but recovery would only be economically feasible if other valuable materials were also recovered simultaneously. Bottom and fly ash from municipal solid waste incinerators may prove to be a promising source, as strong enrichment of Eu, La, Gd, and Tb correlates

with phosphorus pentoxide (P_2O_5) and indicates that the source of REE anomalies in the ash are likely from REE phosphors present in fluorescent materials (15). REEs were found to be present at several orders of magnitude higher in acid mine drainage water than natural water (16) presenting an opportunity to provide a modest but continuous supply of potentially valuable resources as a by-product of otherwise costly remediation activities. Sewage sludge only seems to be a promising source of Gd though (presumably due to its use as a MRI contrasting agent), since other REEs show enrichment factors near unity indicating geogenic origin (17).

The maturation of technologies for recovering REEs from waste streams and recycling them in 'end-of-life' products may result in lower concentrations released into environmental media. However, this must be contrasted against an anticipated exponential growth in their use in consumable products. It is unlikely that the environmental impact of REEs, which seems to be lower than many other metallic elements, will drive increases in recycling and recovery. Therefore, the adoption of technologies to exploit "second-hand" REE resources will likely be dependent on the price of REEs on the global market.

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Article

Neonicotinoids updated

Rowena Fletcher-Wood (Science Oxford)

In a previous issue of the ECG *Bulletin*, the editors wrote about the possible detrimental effects of neonicotinoids on pollinator populations and the impacts on biodiversity and human food security (1). In interviews with Dr Ben Woodcock (Centre for Ecology and Hydrology) and Professor Simon Potts (Reading University), I asked about the evidence supporting a risk to food security, and the role played by bees in pollination.

About 88% of nutritionally important food crops such as fruits, vegetables, nuts and seed crops are pollinated by animals (2). Neonicotinoid impacts on pollination services will thus have widespread consequences for ecosystems and species biodiversity, and also affect human food security. Animal-pollinated plants contribute most of the vitamins and minerals in our diet. Thus, although calorie-containing foods such as wheat and rice are mostly wind pollinated, the nutritional core of our diet could be threatened by falling bee numbers (if bees, which pollinate three quarters of the world's food crops, are representative of other pollinator species).

In his interview, Dr Ben Woodcock explained that he was part of the CEH cohort involved in a large-scale, independent study of neonicotinoid impacts commissioned by pesticide giants Syngenta and Bayer (3). The study took place over one growing season at eleven sites in the UK, Germany, and Hungary, each containing three sets of 40 to 70 hectare oilseed rape fields. The field sizes were a compromise between honeybee foraging ranges and the limits set by regulatory authorities when applying pesticides that were under a temporary ban. In each set of three fields, one field was planted with seeds treated with Clothianidin, the second with seeds treated with Thiamethoxam, and the third with untreated seeds. Six honeybee hives, twelve bumblebee colonies, and fifty cocoons of a solitary Red Mason bee were placed at each site. The study sparked public criticism because of the perceived conflict of interest from using funding from the pesticide giants Syngenta and Bayer. The results have been submitted for peer-review publication.

Simultaneously, Dr Woodcock contributed to a paper that assessed the long-term impacts of field-level doses of neonicotinoids (4). This paper applied statistical methods (multi-species dynamic Bayesian occupancy analysis) to 18 years of UK bee distribution data, spanning 62 species of wild bee and supplied by the Bees, Ants and Wasps Recording Society of the Biological Record Centre. This robust body of qualitative data is collected chiefly by amateur entomologists with specific bee expertise. Bee distributions were correlated against the locations of neonicotinoid-treated oilseed rape and demonstrated a relationship between neonicotinoid use and large-scale loss of populations, particularly among species that forage on oilseed rape.

As Dr Woodcock explained, this second study is a valuable companion to the first because small and large-scale studies only jointly provide results that can elucidate the full impact of neonicotinoids on pollinators. Many field studies are limited to relatively small areas of treated crops for practical reasons and may not capture the full extent of bee-neonicotinoid exposure, as bees can forage over large areas (honeybees regularly forage 2 km from hives). Other field studies are limited to single species. Across time scales of one to two years, natural changes in animal populations, weather conditions and variation in real world agricultural conditions mean that measured responses may be dominated by environmental conditions. On the other hand, laboratory and small-scale field experiments allow better control and replication that is not achievable in larger-scale correlative studies. In the latter case, it is much harder to control for environmental differences, and results are often influenced by a wide range of factors (such as destruction of habitats to produce fields for oilseed rape), many of which are not under investigation. This is a classic problem with correlative studies (3).

In his interview, Professor Simon Potts told me that he was seconded to the UN for two years to co-chair a report on "Pollinators, Pollination and Food Production," which evaluated the global evidence on the causes of pollinator declines and identified effective policy and practice responses to mitigate pollinator losses (5). He also took part in a study assessing the effects of a neonicotinoid on the pollination services that bumblebees provide to apple trees, a crop of global economic significance (2). Under semi-field conditions, pre-exposure of bumblebees to 10 ppb Thiamethoxam

pesticide led to fewer visits to the apple flowers. This not only meant less efficient pollen collection, but also impacted the apple trees, producing fewer seeds. Seeds are considered a key indicator of quality for most apple varieties. The study suggested effects were likely to be on the level of the bee colony, rather than individual bees. This could have serious implications for other crops and ecosystems.

Professor Potts argued that if effects on bees can be extrapolated to other pollinators, these results could have worrying consequences. Loss of pollinators could be a major challenge for global food security, possibly entirely driven by bees. Some foodstuffs like chocolate (primarily pollinated by midges) and coffee on the global market could fall and could return to being luxury, and consumers would more generally have more limited choice and scarcer access to micronutrient rich foods. This could have further sociological effects, dividing consumers between those able and unable to afford these products and increasing the risk of malnutrition amongst lower income earners, especially in developing countries.

Neonicotinoids contribute 80% of the world's seed treatment market and 20% of the world's pesticide market. Many crops that they are applied to, such as oilseed rape, cannot be easily grown organically. The "cabbage" of cereal crops, just about anything eats rape, making it a work-intensive, low-yielding crop to grow without the assistance of pesticides. But this does not mean the effects of neonicotinoids cannot be mitigated. Overall pesticide use can and should be reduced worldwide. Professor Potts and Dr Woodcock recommended an Integrated Pest Management approach that combines pest monitoring with a range of pest control methods, such as crop rotation, field margin management, and biological control (6). This means reforming our paradigm of pesticide use and moving away from continuous prophylactic application to last-resort use only when other strategies are insufficient. Another way to reduce risk is with new technologies, such as reduce-drip nozzles on pesticide sprays to minimise waste and avoid high concentration drops (6).

But these interventions may not enough on their own to protect bees and other pollinators. Professor Potts and Dr Woodcock suggest that ecological intensification of

farming could make a significant difference. This means working alongside biodiversity to increase soil and crop fertility, such as by creating land strips populated by wild flowers and supporting beneficial invertebrates (7). Research suggests that even if you take out 8% of land for these uses, the boost in native biodiversity means a boost in pollination and natural predators like ladybirds that eat aphids, and in turn sustainable intensification of crops – producing just as much product (5). We can also help bees directly by supporting habitats, creating nesting sites and introducing foraging resources that foster more robust populations better able to stand up to the pesticides they do encounter (7).

However, changeover requires work, and farmers are naturally risk-averse. It may be that top down regulatory methods are required to implement ecological farming. Some, like my veg box providers, have turned to organic farming instead, but this has its own problems: organic farming usually requires more land for the same volume of produce and so is less efficient, and as most of our remaining uncultivated land is high value nature sites, these farms would be unable to expand without causing further loss of habitat and

damage to native biodiversity.

So it looks like promoting ecological intensification the key – this doesn't mean banning pesticides, but it does mean encouraging adjacent biodiversity and use smarter technology and methods.

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Honey bees return to their hives. Recent studies have investigated the impacts of neonicotinoid pesticides on honeybees and other insect pollinators. Credit: Fotografiero/Shutterstock

Forthcoming meeting: ECG Distinguished guest lecture and symposium

Inside the engine: From chemistry to human health

When: Wednesday 1 March 2017

Where: Library and Council Rooms, The Royal Society of Chemistry,
Burlington House, Piccadilly, London W1J 0BA

This one-day symposium organised by the Environmental Chemistry Group of the Royal Society of Chemistry explores the chemistry of diesel engines emissions, emissions policy, and how it's affecting human health. The 2017 ECG Distinguished Guest Lecture will be provided by Professor Frank Kelly (King's College London).

Programme

12.00 Lunch and Coffee

13.00 Symposium is opened by ECG Chair Zoe Fleming

Dr Claire Holman (independent consultant) : "Do diesel vehicles cause poor air quality?"

Dr Holman will provide the introduction to the seminar, speaking on the links between diesel and air quality, vehicle regulations and general emissions legislation.

Dr Jacqueline Hamilton (University of York): "Air pollution and traffic: Searching for the missing emissions"

Dr Hamilton will speak on organic compounds from petrol and diesel emissions. Many modern cars emit levels of nitrogen dioxide (NO₂) above regulations when driven under real world conditions. Is this also true for some other pollutants emitted by road transport? These species are much more difficult to measure, but are currently severely underestimated. Do we need to look again at emissions testing and urban monitoring?

14.30 Tea/Coffee and the ECG Annual General Meeting

15.30 Symposium resumes

Mr Simon Birkett (Clean Air in London): "Emissions Policy and Air Pollution"

Mr Birkett will speak on the history of favouring diesel fuel based on CO₂ emissions. He will address issues surrounding emissions surcharges and ultra low emission zones and the opportunity and need to ban diesel, like coal was banned 60 years ago.

ECG Distinguished Guest Lecture 2017:

Professor Frank Kelly (King's College London): "Traffic Pollution and Health in London, Umea and Beijing."

In cities across the globe, road transport remains an important source of air pollutants that are linked with acute and chronic health effects. Professor Kelly will speak on his work over the last 20 years investigating these associations in human challenge chamber studies in Umea, Sweden; real-world exposure scenarios in London and recently the link between traffic emissions and health in the megacity Beijing, China. He will review his group's findings and those from other groups to convince you we need to advance beyond a fossil fuel based road transport system.

17:15 meeting close

Reports on the symposium will be included in the next issue of the ECG *Bulletin* July 2017.

Fees: EARLY BIRD before 1st February 2017: £50/£35 for ECG members (RSC members can join the ECG for free); STANDARD £65/£50

Registration: <http://www.rsc.org/events/detail/24566/inside-the-engine-from-chemistry-to-human-health>



Credit: Olegusk/Shutterstock

Forthcoming meeting

What's new in the analysis of complex environmental matrices?

When: Friday 3 March 2017

Where: Science Suite, Royal Society of Chemistry, Burlington House,
Piccadilly, London W1J 0BA

A joint meeting organized by the RSC's Environmental Chemistry Group, Water Science Forum, and Separation Science Group.

Programme

9.00-9.40 am Registration and coffee

9.40-9.45 am **Graham Mills (University of Portsmouth, UK): Opening and welcome to meeting**

9.45-10.15 am **Leon Barron (King's College London, UK): Screening of complex forensic and environmental samples using high resolution analysis and *in silico* data mining tools**

10.15-10.45 am **Andrew Sweetman (Lancaster University, UK): Use of passive samplers as a potential compliance tool within the EU Water Framework Directive**

10.45-11.15 am Coffee break

11.15-11.45 am **Colin Creaser (Loughborough University, UK): Combining ion mobility spectrometry with mass spectrometry for the analysis of complex samples: the potential for environmental analysis**

11.45-12.15 pm **Stuart Harrad (University of Birmingham, UK): Brominated flame retardants in waste consumer articles**

12.15-1.00 pm (Keynote Lecture) **Jaroslav Slobodnik (Environmental Institute, Slovak Republic): Non-target screening of environmental pollutants in the context of risk assessment of European river basins: the NORMAN network perspective**

1.00-2.15 pm Lunch break and vendors' exhibition

2.15-3.00 pm (Keynote Lecture) **Jacob de Boer (Vrije Universiteit Amsterdam, Netherlands): Human exposure to environmental contaminants: direct probe time-of-flight mass spectrometry reveals a multitude of chemicals indoors**

3.00-3.30 pm **Gavin Mills (Severn Trent Ltd., UK): Advances in the determination of taste and odour compounds in drinking water**

3.30-4.00 pm **Barbara Kasprzyk-Hordern (University of Bath, UK): How can urban water profiling inform our understanding of the state of the environment and public health?**

4.00-4.30 pm **Mark Perkins (Anatune, UK): VOC measurements in ambient air using Selected Ion Flow Tube Mass Spectrometry (SIFT) -MS - automation and calibration considerations**

4.30 pm Roger Reeve (University of Sunderland, UK): Meeting close

Abstracts from the symposium will be included in the next issue of the ECG *Bulletin* July 2017.

Fees: Members £90 (and of BMSS or Chromatographic Society); Non-members £120.00;
Students, retired members and unwaged £25

Registration: www.rsc.org/events/detail/24280/whats-new-in-the-analysis-of-complex-environmental-matrices

Contact: Professor Graham Mills, University of Portsmouth
Dr Roger Reeve, University of Sunderland

Forthcoming meeting

Emerging contaminants in waters and soils – Public health implications

When: 5 April 2017

Where: Royal Society of Chemistry, Burlington House, Piccadilly,
London W1J 0BA

This joint meeting is organised by the RSC's Water Science Forum, Toxicology Group, and Environmental Chemistry Group.

The one-day seminar will discuss the chemistry of Contaminants of Emerging Concern (emerging contaminants), which are those that have recently been discovered in soil and water environments and are considered to be a potential risk to the environment and/or human health.

There will also be poster presentations with this theme, together with a poster prize.

This is the second joint ECG meeting on this topic. For details of the previous meeting please see the July 2015 edition of the ECG *Bulletin*:
http://www.rsc.org/images/ECG-Bulletin-July-2015-final_tcm18-246976.pdf

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An expert analyses takes a water sample to test for contaminants. Credit: Shutterstock

Volatile organic carbons and vapour intrusion

James Lymer (Wardell Armstrong)

The UK, along with other industrialised nations, has a legacy of land contaminated with materials from previous use or naturally occurring sources. Here I outline methodologies for assessing human health risks from volatile organic compounds (VOCs) through indoor inhalation.

VOCs are organic compounds with vapour pressures > 10 Pa; organic compounds with lower vapour pressure are referred to as semi-volatile organic compounds (SVOCs). VOCs can be present on brownfield sites, for example due to poor storage practices or solvent spills. VOCs may be present in the ground beneath existing buildings or on vacant sites intended for redevelopment. Examples of VOCs include non-chlorinated hydrocarbons (e.g. benzene), chlorinated hydrocarbons (e.g. trichloroethene), and nitrogen-, oxygen- and sulphur-containing hydrocarbons (e.g. dimethyl sulphide).

Factors influencing the volatilisation of VOCs into the vapour phase from the subsurface include physicochemical properties that influence the partitioning of the substance into different states, such as vapour pressure and air-water partition coefficient (based on Henry's Law Constant); soil and aquifer properties such as porosity, organic carbon content and permeability; and microorganisms in soil and groundwater.

Indoor inhalation of vapours

Given their high vapour pressures, VOCs have tended to be the main contaminants of concern when assessing the risk to human health via inhalation of vapours from soil and groundwater sources. Elevated indoor vapour concentrations of a hazardous substance can cause chronic and acute health effects, an odour nuisance and/or a flammable hazard. VOCs migrate through the ground via transport mechanisms of advection and diffusion. Vapours accumulate beneath buildings and can migrate inside via cracks in foundations and floor slabs.

Assessment methodologies

An assessment of the risk to human health from vapour intrusion incorporates several considerations, including source properties (toxicity and physicochemical parameters of the substance or substances), pathway properties (site measurements, vapour modelling approach, soil and aquifer properties, vertical/horizontal distance between source and receptor), and receptor properties (building design, resident, worker).

UK: Contaminated land exposure assessment (CLEA)

The Environment Agency CLEA model (1) has been developed to derive assessment criteria for soil contaminants. It incorporates multiple exposure pathways, including the inhalation of vapours. The CLEA model can be used to derive separate assessment criteria for the inhalation of vapours pathway only.

An Environment Agency (EA) review of models for predicting vapour intrusion into buildings (2) recommended that an approach based on the Johnson and Ettinger (J & E) screening model should be included in the CLEA model (3). The J & E model uses a one-dimensional analytical solution to diffusive and advective transport of vapours and calculates an attenuation factor that relates steady state gas concentrations at the source to indoor air concentrations based on soil and building characteristics. It has a number of simplifying assumptions regarding contaminant distribution and occurrence, subsurface characteristics, transport mechanisms and building construction and design (3). The J & E model is generally recognised to be over-conservative in many cases, particularly as it assumes no degradation or source reduction over time.

United States: Environmental Protection Agency (EPA)

The US EPA has produced technical guidance on the vapour intrusion pathway (4), including a database of vapour concentrations recorded at sites in the USA. It has developed a tool to derive vapour intrusion screening levels (VISL) for groundwater, soil gas and indoor air in default exposure scenarios (5). The values derived by the VISL tool are based on a generic

conceptual model, which assumes a groundwater or unsaturated zone source of vapours that diffuse through unsaturated soils toward the surface and into buildings, the occupiers of which are the receptors. It is assumed that sub-surface conditions will reduce or attenuate vapour concentrations as vapours migrate toward the building, and that dilution of vapours will occur as they mix with air in the building.

The screening levels are used to assist in determining whether volatile substances in the subsurface pose a risk to human health via the vapour intrusion pathway. They are not intended to be used as clean-up levels or remediation targets. The tool allows for the derivation of site specific values.

Site measurements

Typically in the UK, soil and groundwater samples are analysed for VOCs during routine intrusive site investigation works. An initial vapour intrusion assessment can then be carried out by comparing these concentrations with generic assessment criteria (GAC). This approach is focussed on characterising the VOC source area and is limited by the use of generic screening tools, with no site-specific conditions such as inclusion of preferential pathways or degradation of vapours.

Site measurements can also be taken to support a more detailed assessment and reduce uncertainty by providing insight into actual site vapour conditions. These measurements may include soil vapour sampling, sub-slab vapour sampling (taken beneath floor slab or foundations), and indoor air measurements.

These techniques are intrusive and can be problematic if there are occupier concerns and access constraints. Indoor air measurements can be influenced by background VOC concentrations from sources such as cleaning fluids, furnishings, and cigarettes. The analytical methods should be appropriate for comparison with relevant target concentrations in air. At vacant sites where the proposed buildings are not yet in place, site measurement possibilities are more limited; for example, soil vapour samples may not be representative of vapour concentrations under future buildings and sub-slab and air sampling is not possible prior to construction.

Documents published in 2009 and 2012 present a UK-based approach to the investigation, monitoring and remediation of VOCs in ground (6, 7).

Non-chlorinated and chlorinated hydrocarbons

Vapour intrusion can be a key pathway for human health exposure from chlorinated and non-chlorinated hydrocarbons (8). Volatile petroleum hydrocarbons tend to readily biodegrade under aerobic environmental conditions if sufficient oxygen and microbes are present, whereas volatile chlorinated hydrocarbons tend to biodegrade much more slowly and prefer anaerobic conditions.

Mitigation

Conventional remediation techniques such as excavation and *ex situ* treatments (biological, physical, and chemical) may be appropriate to reduce the VOC concentrations at vacant sites prior to redevelopment. Alternatively, the design of the proposed buildings can incorporate mitigation measures such as sealing cracks in foundations, installing vapour membranes, depressurisation and venting.

An assessment of the risk to human health from vapour intrusion incorporates several considerations, including source, pathway, and receptor properties.

Mitigating VOC contamination beneath existing buildings can be problematic and more expensive than at redevelopment sites. Reasons include likely limited access to the source area, limitations and cost of *in situ* techniques for removing VOC contamination beneath the building (such as soil vapour extraction and air sparging), and difficulties with retrofitting a passive membrane to an existing building.

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Non-aqueous phase liquids: properties, risk reduction and remediation

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The term non-Aqueous Phase Liquids (NAPLs) describes a class of organic liquids that are immiscible with water. NAPLs are among the most common organic contaminants in the sub-surface environment as a result of their ubiquitous use, accidental release during handling or transport, leakage from storage tanks, and poor disposal practices.

The key defining properties of NAPLs are their chemical composition, density, wettability and interfacial tension, viscosity, solubility, and vapour pressure. Density is particularly important, as NAPLs are usually further categorised as Light NAPLs (LNAPLs), which are less dense than water, and dense NAPLs (DNAPLs), which are denser than water. The most common LNAPLs are fuels and oils, such as petrol (gasoline), diesel, heating oils and jet fuel (kerosene). Typical DNAPLs include chlorinated solvents, coal tars and polychlorinated biphenyl oils.

Environmental Behaviour

When an NAPL is introduced into the soil environment it normally migrates downward. The path taken can, however, be quite complex and depends on the pore or fracture size of the soil and the concomitant capillary forces generated when the NAPL comes into contact with water in the soil's unsaturated zone and at the water table. LNAPLs normally cannot penetrate below the water table because of buoyancy forces, although a sufficiently large LNAPL mass will depress the water table. DNAPLs, on the other hand, can and very often do penetrate the water table.

At the trailing edge of the NAPL body, NAPL droplets (termed residuals and encountered as blobs or ganglia stretching through several pore spaces) become detached and are normally held in these pore spaces by capillary forces. This happens both in the unsaturated and saturated zones of the sub-surface environment. In

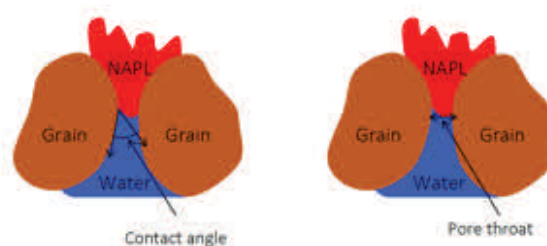


Figure 1. The contact angle and pore throat size play key roles in the dynamics of NAPLs through soils.

the unsaturated zone, vaporisation of NAPL components produces a mobile contaminant plume in the vapour phase. Residuals in the unsaturated zone may also dissolve in infiltrating rainwater, which eventually provides a source of groundwater contamination. In the saturated zone, NAPL residuals slowly dissolve in flowing groundwater to create a contaminant plume.

Capillary Forces

The entry of a NAPL into an air- or water-filled pore or fracture is determined by two important pressure terms. The first is the capillary pressure, P_c , which is defined by the following equation:

$$P_c = P_{nw} - P_w \quad (1)$$

where P represents pressure and the subscripts c , nw , and w refer to capillary, non-wetting, and wetting, respectively. A wetting fluid is one that spreads over a surface in competition with another fluid. In soils and rocks, water is usually the wetting fluid when in competition with a NAPL. However, when in contact with air, NAPLs are the wetting fluids.

Wetting behaviour is characterised by the contact angle (Figure 1). The contact angle is the angle made by a tangent to the non-wetting fluid and the solid surface proceeding from the point where the three phases come

into contact. This contact point is in reality a contact line when viewed in three-dimensional space.

The second pressure term is the entry (or displacement) pressure, P_e , and is given by the Laplace equation:

$$P_e = 2\sigma \cos(\theta)/r \quad (2)$$

Here σ is the interfacial tension between water and the NAPL, θ is the contact angle, and r is the pore throat radius. The contact angle term appears as a cosine term. If θ is 0° then the cosine term is 1. On the other hand, a contact angle of 90° gives a cosine of zero, implying that a positive entry pressure only arises at a curved interface. For the NAPL to displace water from a pore, the following inequality must hold true:

$$P_{nw} > P_w + 2\sigma \cos(\theta)/r \quad (3)$$

Thus, in soil media with large grain size, the entry pressure is small and NAPLs—especially DNAPLs—tend to displace water from pores. On the other hand, in locations with small grain sizes NAPLs find it far more difficult to displace water. Thus, if a highly permeable layer (such as sand) overlays a less permeable layer (such as silt or clay), NAPLs will migrate vertically downward in the top layer but then migrate horizontally when encountering the bottom layer. Identifying the migration pathway of a NAPL therefore requires a good understanding of sub-surface lithology.

Solubilisation and vaporisation

Key concerns after a NAPL spill are its impacts on the environment and the resulting liabilities of site owners where the release has occurred. Density and viscosity control the length of time during which a NAPL body will remain mobile. Chlorinated solvents have high densities and low viscosities therefore do not remain mobile for long. In contrast, creosotes and coal tars have densities only slightly greater than that of water and large viscosities and can therefore continue to migrate for considerable periods of time.

The partial pressure of NAPL components in the vapour phase of the unsaturated zone is an important risk driver for contaminant migration to off-site targets. In the absence of a complete understanding of the physical chemistry of a NAPL mixture, it is generally assumed that Raoult's Law gives the partial pressure, p_i , of a component in the vapour phase:

$$p_i = x_i p_i^{sat} \quad (4)$$

Here, x_i is the mole fraction of component i and p_i^{sat} is the saturated vapour pressure of component i . Clearly, low

molecular mass components with low boiling points are particularly mobile in the vapour phase.

Raoult's Law is also used to estimate component solubilities, using an analogous equation to equation 4 where s refers to the solubility:

$$s_i = x_i s_i^{sat} \quad (5)$$

The reader should begin to understand from the forgoing discussion that although NAPL releases result in the creation of a contaminant source zone, it is the appearance of NAPL components either in the vapour or aqueous phase that is usually first detected and that provides the background to environmental risk assessments.

Risk Reduction and Remediation

Removal of the source or breaking the pathway can be used to reduce chemical hazard exposure to acceptable limits. For LNAPLs like petroleum, vapour phase extraction is very often effective for source removal. For example, vacuum enhanced recovery techniques rely on the vaporisation of volatile LNAPL components from the organic liquid phase and volatilisation of components from the water phase. Additionally, application of a high vacuum to the sub-surface induces air to enter, which provides fresh supplies of oxygen and thereby aids the biodegradation of the hydrocarbon components present in the source zone. For chlorinated hydrocarbon solvents (DNAPLs), some success has been achieved with the joint application of an electron donor system (emulsified soya oil, methanol and lactate) and a halo-respiring bacterium. Other approaches have been used depending on the location and type of NAPL spill (1, 2).

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