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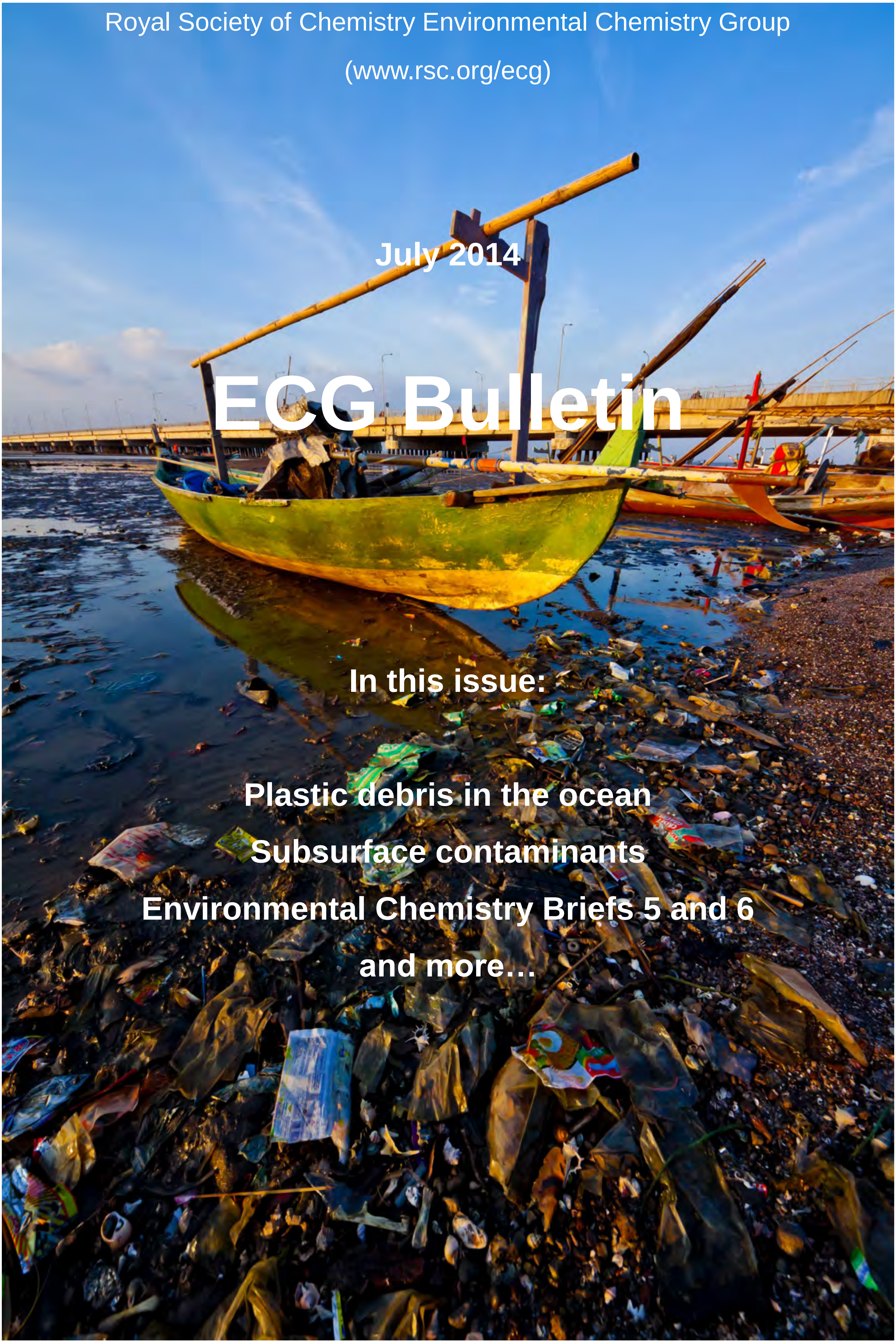

July 2014

ECG Bulletin

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This and previous issues of the ECG *Bulletin* are available without charge online at www.rsc.org/ecg.

Update

Status of global climate

2013 tied with 2007 as the sixth-warmest year since records began in 1850, with record warmth in Australia and near-record-high temperatures in Argentina and New Zealand. Typhoon Haiyan and Cyclone Phailin were among the strongest storms ever to make landfall, while droughts hit parts of Africa, China, and Brazil. These and other climate extremes are discussed in the annual statement on the status of the global climate in 2013, published by the World Meteorological Organization (WMO) on 23 March 2014 (1). The report is based on datasets made available to the WMO by its members and partners, and is peer reviewed.

In a separate chapter, Sophie C. Lewis and David Karoly analyse the likely contributions made by natural causes and human-induced climate change to the extreme record-high temperatures in Australia. Based on a suite of climate model simulations involving nine different models, they show that human-induced climate change increases the likelihood of extreme summer temperatures in Australia five-fold (2) and that the record-high temperatures for the whole year of 2013 are almost impossible to reproduce in models without human-induced climate change.

1. See www.wmo.int/pages/mediacentre/press_releases/pr_985_en.html. The full report may be accessed at https://docs.google.com/file/d/0BwdvoC9AeWjUeEV1cnZ6QURVaEE/edit.
2. S. C. Lewis, D. Karoly, "Anthropogenic contributions to Australia's record summer temperatures of 2013", Geophysical Research Letters **40**, 3705–3709 (2013).

The ECG Bulletin *Editors*

Update

Outdoor air pollution

The vast majority of cities that report air quality data do not meet World Health Organization (WHO) air quality guidelines. And the air pollution experienced by about half of the urban population being monitored is at least 2.5 times higher than the WHO-recommended levels, putting people at additional risk of serious, long-term health problems. These are some of the conclusions from a database published by the WHO on 7 May 2014 (1).

The database covers *ca.* 1600 cities from 91 countries around the world for which particulate data are available on PM_{10} (particulate matter at 10 micrometres or less) or $PM_{2.5}$ (2.5 micrometres or less). $PM_{2.5}$ is considered to be the most reliable indicator of health risks from air pollution. Around 500 more cities are included than in the previous assessment in 2011, reflecting an increase in air quality monitoring. However, in many cities air quality has deteriorated. There is a lack of data for some medium or low income regions, particularly in the Eastern Mediterranean and Africa.

Earlier this year, the WHO warned that about 7 million deaths worldwide in 2012 (about one in eight of total global deaths) were linked to indoor and outdoor air pollution; an estimated 3.7 million of these deaths are attributed to outdoor air pollution (2).

1. See http://www.who.int/mediacentre/news/releases/2014/air-quality/en/. The database may be found at http://www.who.int/phe/health_topics/outdoorair/databases/cities/en/
2. See http://www.who.int/mediacentre/news/releases/2014/air-pollution/en/

The ECG Bulletin *Editors*

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Update

Human health exposure from contaminated land: A DEFRA report

James Lymer (Wardell-Armstrong)

A new classification system aids the assessment of risk to human health from exposure to contaminated land in the UK. This article explains the methodology.

In April 2012, DEFRA (Department for the Environment, Food and Rural Affairs) introduced a new, four-category system for classifying land under Part 2A of the Environmental Protection Act for cases of a significant possibility of significant harm to human health. Land is determined as contaminated under Part 2A if it falls within Categories 1 or 2; Category 4 includes land where the level of risk posed is acceptably low. To support the assessment and classification of land within these categories, DEFRA commissioned a research project to develop a methodology for deriving Category 4 screening levels (C4SLs) and recommend values for six substances. The project was awarded to a research team led by CL:AIRE (Contaminated Land: Applications in Real Environments).

Following publication of the CL:AIRE report in December 2013 (1), DEFRA issued a policy companion document in March 2014, outlining a methodology for deriving C4SLs and providing recommended C4SL values for six substances: arsenic, benzene, benzo(*a*)pyrene, cadmium, chromium(VI), and lead. These values were derived for four generic land uses: residential, commercial, allotments, and public open space.

Category 4 Screening levels describe a level of risk that, although above minimal, is strongly precautionary. Soil guideline values (SGVs) and other generic assessment criteria (GAC) are derived at a risk that is considered to be minimal. Therefore, C4SLs describe a higher level of risk than do SGVs and GAC. C4SLs are intended not only for use in the Part 2A system but also as generic screening criteria for land development planning within a generic quantitative risk assessment (GQRA).

Methodology

The methodology for deriving C4SLs is based on the Environment Agency, Contaminated Land Exposure Assessment (CLEA) model used to derive the SGVs (2, 3). A more pragmatic approach was adopted in selecting parameters for the CLEA model to derive C4SLs compared to the derivation of SGVs. The approach included modification of the toxicology and/or the exposure parameters used in the model. To address uncertainty in the parameters used, a sensitivity analysis was also undertaken as part of the C4SL derivation. For the SGV derivation process, the toxicology input (health criteria values) is an estimated contaminant concentration that would pose a tolerable or minimal risk to human health. For the C4SL derivation process, the toxicology input (low level of toxicological concern or LLTC values) is the estimated concentration of a contaminant that would pose a low risk to human health.

An example of a C4SL

Inorganic arsenic compounds are considered carcinogenic both *via* inhalation and ingestion, and it is classed as a non-threshold contaminant. The CLEA model is used to estimate the average daily exposure from arsenic in soil, which is equivalent to its toxicity value. This is reported as a soil concentration that represents a low risk to long term human health, known as a C4SL. Recommended arsenic C4SLs are: residential (with home-grown produce), 37 mg/kg; residential (without home-grown produce), 40 mg/kg; allotments, 49 mg/kg; commercial, 640 mg/kg; public open space 1, 79 mg/kg; public open space 2, 168 mg/kg. Further details on the derivation and application of these values are presented in the main SP1010 report and companion document, and in the CLEA framework reports.

References

1. DEFRA, SP1010 – Development of Category 4 Screening Levels for assessment of land affected by contamination, published on 20 December 2013.
2. Environment Agency, *CLEA Reports*: see https://www.gov.uk/government/collections/land-contamination-technical-guidance
3. Previous ECG *Bulletin* articles on contaminated land may be found in the July 2008 issue (pp 18-20) and the January 2010 issue (p 36).

The author is Chair of the ECG.

Meeting report

Organic chemistry and toxicology of contaminants in the ground

James Lymer (Wardell-Armstrong) and Kate Jones (Health and Safety Laboratory)

This is a report of a meeting jointly organised by the RSC Toxicology Group and the RSC Environmental Chemistry Group, with support from RSC's Environment, Sustainability and Energy Division, which was held at the Chemistry Centre, London on 13 February 2014.

The aim of the meeting was to present a range of perspectives on the chemistry and toxicology of chemicals in the environment. Fifty-four delegates attended from a wide range of organisations, including consultancies, regulators, and academia. Copies of the presentations from the speakers are available from the ECG website (www.rsc.org/ecg).

There are two main groups of environmental contaminants:

Common environmental contaminants are substances with known chemical and toxicology properties (such as trichloroethene) that are present in the environment generally due to a historic lack of regulation, poor use, storage practices, and waste disposal and are now subject to remediation in soil and groundwater systems. These substances are now largely banned from use (e.g. polychlorinated biphenyls, PCBs) or are tightly regulated for use by operators and in their treatment/disposal by waste companies (Environmental Permitting Regulations 2014) and hence are less likely to enter the environment.

Contaminants of emerging concern are substances not previously considered or known to be significant in the environment. These contaminants, which, for example, include pharmaceutical and personal care products, may have no regulatory standard. Due to improved monitoring techniques and increasingly sensitive analytical methods, more emerging contaminants are being detected.

In the developed world, there has been a gradual decrease in the concentrations of common environmental contaminants, such as heavy metals, polychlorinated biphenyls, dioxins, and polycyclic aromatic hydrocarbons (PAHs). This improvement is largely due to stricter regulations with improved monitoring, cleaner industrial processes, and better waste disposal practices. There is now a focus on contaminants of emerging concern. **Eric J. Weber** (United States Environmental Protection Agency, Athens, Georgia) began the meeting with a presentation entitled "*The Environmental Fate Simulator: A tool for predicting the degradation pathways of organic chemicals in groundwater aquifers*." Eric's research is currently focused on elucidating reaction pathways for the reductive transformation of organic pollutants in anoxic systems, and understanding how organic pollutants with reactive functional groups (such as aromatic amines) covalently bind to aqueous and sediment-associated natural organic matter. Eric highlighted the need for a systematic method for updating fate and transport models with the latest research concerning transformation and transport of organic chemicals.

The Environmental Fate Simulator (EFS) is a computational tool that screens organic chemicals for possible routes of human and ecological exposure and compiles all available data on chemicals and chemical processes. Access is provided to databases and environmental fate and transport models that can estimate concentrations of chemicals and their transformation products in soil and aquatic ecosystems. The EFS uses the knowledge of chemical structure and environmental conditions to predict the reaction rates, mechanisms and partitioning behaviour of organic contaminants in the environment. Upon release of the EFS, the major impact of this work will be to reduce the uncertainty in exposure assessments by incorporating the most robust process science available for predicting chemical transport and transformation.

Marianne Stuart (British Geological Survey, Wallingford) next spoke on "*Emerging organic groundwater contaminants and their transformation products*." Marianne's research interests include emerging contaminants and impacts of hydraulic fracturing. The pesticide Atrazine is the most common contaminant in

UK aquifers. Other emerging contaminants include pharmaceuticals, industrial additives and by-products, personal care products, and flame/fire retardants. Many of these contaminants are currently unregulated and some can have human or ecological health effects. Many emerging contaminants are relatively small polar molecules, which are not effectively removed by conventional drinking water treatment using activated carbon. Those with an octanol-water partition coefficient (log K_{ow}) below 3 can potentially persist in the supplied water. There is a need for a better understanding of their fate in environmental systems.

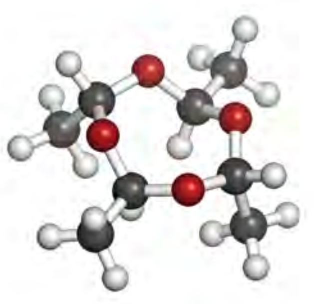

Image credit: Shutterstock

Metaldehyde (acetaldehyde tetramer) (a molecular model is shown right; oxygen atoms in red) is an example of a compound that has relatively recently emerged as a groundwater contaminant. It is a selective pesticide used to control slugs. First introduced in 1940, it has been widely used in agriculture, horticulture, recreational land, and gardens since the 1970s. A new method for measuring metaldehyde concentrations enables this substance to be monitored in drinking water supply catchments. Marianne also briefly discussed potential contaminant sources in onshore fracking, including flowback water and the chemical mixture in fracking fluid. There is a move toward use of less harmful chemicals in fracking, and fracking fluid chemicals in the UK will be tightly regulated.

Alex Stewart (Public Health England) and **George Kowalczyk** (WCA Environment) spoke on "*Disposal, discovery and disruption: subsurface vapour transport and impacts of chlorinated solvents in a local community*", reporting a case study of hexchlorobutadiene (HCBD) contamination and its dispersion into homes in the Central Liverpool area.

Houses had been built on a disused landfill site. Levels of up to 6.8 ppb of HCBD were detected in 26 homes, compared to a reference level of 0.6 ppb (recommended by the UK's Committee on Toxicity, COT). HCBD causes kidney damage through metabolism to the active toxic species. George presented three approaches to determining a "safe" cut-off for HCBD, including the COT methodology, a PBPK (physiologically based pharmacokinetic modelling) approach based on point of departure, and a benchmark dose approach. The COT and benchmark dose approaches gave similar, very low limits (<0.6 ppb), whereas the PBPK approach gave an acceptable level of 56 ppb. This difference results from the fact that the PBPK approach takes into account several key metabolic differences between rats (the source of the available toxicology data) and humans.

As the levels detected in homes exceeded the COT reference level, the "polluter pays" concept was enforced, the houses were demolished, and the residents re-housed. Glutathione-*S*-transferase (GST, a marker, *inter alia*, of distal tubular cell damage) was found to be raised in over half of the residents tested. In a later round of testing after relocation, the number of raised findings had dropped to 18% of residents tested. These data suggest that some residents may have been exposed to something that has affected their kidney function; however, the tests are not specific to HCBD and the geographical area in question has a higher than average incidence of renal disease anyway. Engaging with the community and relevant stakeholders was key in managing an emotive and stressful situation for the residents concerned.

Tony Fletcher (LSTHM) ("*Human exposure, body burdens and health effects of PFOA and PFOS*") presented results from the C8 study (also known as the perfluorooctanoic acid or PFOA study) of contaminated groundwater in the Mid-Ohio Valley, USA. This was a large class action legal case, and the settlement mandated installation of activated carbon filtration, the establishment of a health project to undertake a baseline survey of clinical markers of exposure, and the formation of a science panel to undertake epidemiological research to determine any links between exposure to PFOA or PFOS (perfluorooctanesulphonic acid) and disease.

Blood biomarkers were measured and questionnaires obtained from over 69 000 people. PFOA levels were, on average, 20 times higher than background levels, with large differences in levels depending on the geographical area of residence. The health project modelled the historical exposure in the valley (subsoil and well concentrations) using air and water data going back to 1950. Serum PFOA levels were also modelled historically from current measured levels. The science panel looked at the association of PFOA exposure with a number of diseases (12 categories of disease, including 21 different cancers). Six probable disease links were found (preeclampsia, colitis, thyroid disease, testes and kidney cancers, and high cholesterol). Tony gave case studies of two of these links, cholesterol and kidney disease. Profiles over time and excretion patterns were important in determining links to disease. It was stressed that care must be taken in inferring causal associations from cross-sectional biomarker studies.

Alistair Boxall (University of York) gave a presentation entitled "*Side effects of medication in the soil environment.*" Alistair's research focuses on emerging and future ecological and health risks posed by chemical contaminants in the natural environment. In his talk, he discussed the common sources and pathways of pharmaceutical migration in the soil environment, including land spreading of manure from livestock animals, wastewater treatment effluent into surface water/soil, and inappropriate disposal of medical waste. Pharmaceuticals are designed to be biologically active and are thus likely to affect organisms in the environment. Examples of pharmaceuticals in soils include antibiotics, anti-parasitics, and anti-depressants. Alistair discussed a study in which a small area of agricultural soil was treated with manure containing pharmaceuticals to determine the run-off concentrations, with samples taken pre- and post-application. Experiments have shown that the uptake of pharmaceuticals from soil by earthworms and plants is affected by soil properties.

The risks to human health from pharmaceuticals in soil are considered to be low, although subtle effects are seen in organisms. The concentrations of some pharmaceuticals may be high enough to affect terrestrial organisms, although our understanding is much less developed than that of the aquatic environment.

Graeme Paton (University of Aberdeen) spoke on "*Fractionating hydrocarbons for hazard and risk assessment; chemical and biological analysis*". Graeme's research includes fate of inorganic and organic pollutants in the environment, development of bioassays to assess environmental toxicity, and chemical and biological techniques for soil remediation. He outlined the use of chemical, biological, and ecotoxicological testing to decide whether contaminants such as weathered petroleum hydrocarbon mixtures pose a risk to human health, groundwater and surface water, or ecosystems. The chemical analysis method for isolating petroleum hydrocarbons uses an acetone:hexane solvent and ultrasonic extraction followed by fractionation *via* a silica column and gas chromatography–mass spectrometry.

Human health screening values are derived using the Environment Agency CLEA (Contaminated Land Exposure Assessment) model for comparison with soil concentrations to determine risk to human health. Methods of assessing the risk to controlled waters (surface water and groundwater) are well established through use of groundwater risk assessment models such as ConSim and Remedial Targets Methodology (Environment Agency). Fugacity models can be used to establish the general partitioning behaviour of petroleum hydrocarbons in soil, which tend to have a preference for the soil and non-aqueous liquid phases.

Over time, petroleum hydrocarbons will age and the bioavailability (as a function of degradation and toxicity) will change, with the proportion of the non-bioavailable fraction increasing with time as the bioavailable fraction is degraded. The toxicity may increase and then decrease in association with biodegradation. The change in concentration with time was demonstrated with soil samples impacted with different hydrocarbon source types and concentrations. Also indicated was whether the concentrations posed a risk to human health, controlled waters or ecology with or without the application of bio-remediation using biopiles or windrows. The remainder of the presentation was a discussion on the remediation decision tool and its application to several case studies.

Image credit: Shutterstock

Robert Kalin (University of Strathclyde), in his talk on "*Environmental forensics with GCxGC TOFMS analysis*", gave an overview of two-dimensional gas chromatography time-of-flight mass spectrometry. This technique takes the separation output from one column and re-separates it on a second column, giving much improved resolution of the components of complex mixtures. The technique can identify thousands of components, which can be classed into chemical groups within the contour plot that is produced. Robert gave an example of PCB contamination in storm petrels – wrecked seabirds recovered from Canada and the UK showed different PCB signatures, primarily due to different food chains. A second example, identifying sources of coal tar, was used to demonstrate the resolution of the technique. Phenanthrene and anthracene, despite having the same molecular mass, were demonstrated to be physically resolved (as were fluoranthrene and pyrene). Using multivariate statistical methods, it was possible to identify the source of unknown coal tars compared to a number of known standards (such as horizontal or vertical retort, creosote, coke ovens). Such "fingerprinting" could prove invaluable in environmental forensic cases seeking to identify polluters.

James Lymer *is the Chair of the RSC's Environmental Chemistry Group.*

Kate Jones *is the Chair of the RSC's Toxicology Group.*

Meeting report

Soft ionisation mass spectrometric techniques and the environmental sciences

William Bloss (Birmingham University)

On 20 November 2013, the Environmental Chemistry Group and the Molecular Physics Group of the Institute of Physics co-organised a half-day meeting on mass spectrometry (MS) techniques in the environmental sciences, which was held at the University of Birmingham.

The meeting was structured around four talks from invited speakers, with plenty of time for questions and discussion. **Professor Jonathan Williams** (Max Plank Institute for Chemistry, Germany) first spoke on "*The atmospheric chemistry of forests, a forgotten molecule, and a football match*". He described a series of recent field measurements investigating volatile organic compound (VOC) emissions over the boreal forest in Hyttialla, Finland, and the identification of a somewhat overlooked atmospheric C—O compound, carbon suboxide (C_3O_2, O=C=C=C=O). This compound is thought to be associated with biomass burning, but makes only a modest overall contribution to atmospheric VOC loading. The final aspect of his talk concerned measurements of the atmospheric composition in the open-roofed stadium of a local football team, FSV Mainz 05, during a match against VfL Wolfsburg, as a convenient setting for monitoring emissions associated with human activity (or at least, that subset of the population represented by German football fans). Substantial signals for ethanol, acetonitrile (smoking), and ozonolysis products (skin oil) were identified. Unfortunately, neither team scored a goal during the match in question; the opportunity to monitor any transient signal associated with mild euphoria thus did not arise.

The second speaker, **Dr Emily House** (Lancaster University), reported on her recent work characterising within- and above-canopy VOC emissions in a talk entitled "*Measuring fluxes of biogenic volatile organic compounds above the Amazonian rainforest using PTR-MS*". The talk led to a lively discussion of the difficulties of characterising and working with long inlet lines. The meeting then took a slight change of emphasis, with **Professor Paul Thomas** (Loughborough University) talking on "*Does it have to be blood sweat and tears? Non-invasive approaches to therapeutic measurements, and emergency medicine*". Paul described the use of differential ion mobility spectroscopy coupled to thermal desorption gas chromatography in a suitcase-sized experiment for a series of physiological assessments including stress responses. The final speaker, **Professor Armin Wisthaler** (University of Innsbruck/Norwegian Institute of Air Research), gave a comprehensive summary of soft ionisation methodologies under the title "*An overview of on-line CIMS methods for the measurement of organic trace gases in the Earth's atmosphere*". He concluded with a discussion of future research priorities and possible directions. Key areas included a likely focus on time-of-flight mass separation (rather than quadrupole sensors), implementation of multi-dimensional MS-MS approaches, and the use of novel ion chemistries to exploit – or suppress – impacts of secondary chemical interactions.

The chemistry of forests. *At the meeting, Professor Jonathan Williams reported on measurements of volatile organic compounds above boreal forests in Finland. Image credit: Shutterstock*

The meeting was attended by about 55 delegates. It followed on from a successful previous meeting on the same topic in 2012, also held in Birmingham (see ECG *Bulletin*, February 2013, pp 13-14). It was agreed to hold a third meeting in the autumn of 2014, potentially hosted by the University of Lancaster.

The author is Vice-Chair of the ECG.

Meeting report

Plastic debris in the ocean — a global environmental problem

Rowena Fletcher-Wood (Birmingham University) and Stephen Ball (Leicester University)

The ECG Distinguished Guest Lecture and supporting talks link fundamental chemical science with a current environmental issue. This year's topic was plastic debris in the ocean. The meeting, which took place on 12 March 2014 at Burlington House, London, was organised by Stuart Wagland (ECG committee member) and jointly chaired by William Bloss and James Lymer (respectively, the retiring and incoming Chairs of the ECG committee).

The meeting's first speaker was polymer chemist **Norman Billingham** (Emeritus Professor, University of Sussex), who spoke on "*Polymers and their environmental degradation*" and declared himself tasked to "cover the whole of polymer chemistry in about forty minutes". He began by reviewing the different types of polymers (thermoplastics *versus* thermosetting; amorphous *versus* semi-crystalline) and their production methods, noting that chemically identical polymers can be produced from monomer precursors derived both from fossil fuels and sustainable sources such as bioethanol. Thus the distinction between an environmentally costly and an environmentally friendly plastic is blurred. Next Professor Billingham tackled the degradation routes for plastics in the environment and sought particularly to address the fallacy that "all plastics that have ever been made are still with us today". Any polymer will eventually degrade, but much depends on the conditions. Oxidation is the most likely degradation route in the environment, but most polymers today contain additives to stabilize them against oxidation. The long carbon chains of polyethylene are devoid of chemical functional groups and are particularly resistant to biodegradation by microorganisms, which typically initiate the breakdown of polymers by a combination of depolymerisation and enzymatic hydrolysis.

It is, of course, possible to engineer plastics to be more amenable to biodegradation by, for example, incorporating hydrolysable ester linkages into the polymer chain. However, doing so typically compromises the physio-chemical properties of plastics that makes these materials so good at their job (mechanical strength, chemical stability, being impervious to gas and moisture). The key problem is that the very properties you want for biodegradability are the ones that you do not want in a durable packaging material. Indeed, the term "biodegradable" is itself somewhat misleading.

Image credit: Shutterstock

Strictly, biodegradable packaging is required to meet European Standard EN13432, such that shredded plastic pieces degrade under industrial composting at temperatures above 50 °C. Such conditions do not occur in the environment.

Not much is known on the specific question of how plastics degrade in seawater. It is reasonably well established that ultra-violet light and higher temperatures accelerate the degradation of plastics (the response is approximately linear with light intensity and exponential with temperature). The cooling effect of seawater is therefore likely to slow down degradation. Plastics that have sunk beneath the water, away from light and oxygen, are likely to be extremely long-lived.

Edwin Foekema (Institute of Marine Resources and Ecosystem Studies, Netherlands) discussed the impacts of microplastics on marine life in his talk "*Aspects that determine the actual risk of plastic associated POPs for marine organisms.*" Persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), dioxins and DDT are highly toxic and/or carcinogenic. POPs are only sparingly soluble in water, but readily dissolve in plastics, such that trace amounts in seawater concentrate in plastic debris in the ocean. When ingested by aquatic life, POPs migrate to lipid environments such as the tissues of the organisms. A Japanese study has shown that plastic fragments collected from beaches around the world contained varying but consistently elevated concentrations of POPs [Ogata *et al.*, *Marine Pollution Bulletin*, **58**, 1437, (2009)]. If the plastic pieces are sufficiently small, they can be ingested by indiscriminate eaters like lugworms that provide food for species further up the food chain, including fish species that we humans enjoy eating. Inside the lugworm's gut, phase equilibria re-partition the POPs between the plastic and the organism's tissues (the lipid phase), wherein they bio-accumulate. The problem is not that the plastic particles are intrinsically harmful to marine organisms (although chemical components that leach out of the plastic can be), but rather that the particles provide an efficient mechanism through which harmful POPs are pre-concentrated and transported into the organism.

Heather Leslie (Vrije Universiteit, Amsterdam, Netherlands) began her talk on "*Macroplastics and microplastics – what is their environmental impact?*" with an overview of the different size fractions of plastic litter in the oceans. Macroplastics comprise the large pieces of packaging, drinks bottles, fishing nets and ropes commonly seen washed up on the shoreline. Whether by chemical degradation, biodegradation or the mechanical action of the sea, macroplastics are broken down into smaller pieces. These fragments are re-categorised as microplastics once the particle sizes become smaller than about 5 mm (awkwardly, different research groups adopt different sizing conventions, which is a significant issue hindering comparisons between observational datasets). There is no minimum size limit to microplastics; particles have been found down to a diameter of 1 μm, and Heather expects there to be even smaller particles (as yet undetectable) circulating in the environment. Large macroplastic items, she argued, are "only young microplastics" since the former will inevitably be reduced to the latter.

Plastic litter in the ocean is part of a very dynamic system. Ocean currents move plastics around the globe: for example, debris washed into the sea by the tsunami that struck Japan on 11th March 2011 began to wash up on the west coast of the United States in Spring 2013 – see http://marinedebris.noaa.gov/tsunamidebris/faqs.html. Whilst at sea, plastics might degrade, sink, degrade further, re-float, be colonised by biota (which might also sink the plastic or, by covering its surface, protect it from degradation); all of these processes repeat many times. Meanwhile, residual monomers or chemical components added during manufacture to give plastics their desirable properties (plasticisers, UV stabilisers, pigments, flame retardants) are slowly released into the environment.

A handful of studies have identified specific toxic effects in marine species that have come into contact with microplastic debris. However, because "every plastic degrades with its own personality", the toxic effects remain largely unknown as plastics degrade and move through the environment. The consensus opinion is that microplastics are "sub-toxic" since, although microplastic particles are liable to impair the functioning of an organism that has ingested them, the organism itself probably will not die. That said, the effects of microplastics are endemic because many other individuals from the same population will also have come into contact with, and probably also ingested, similar plastic particles. If, however, a large marine organism becomes entangled with a piece of macroplastic debris, it is likely to be fatal. This is obviously very unfortunate for the individual creature, but the rest of the population is not harmed.

The EU-funded FP7 CleanSea project is developing a roadmap to "good environmental status" for marine litter by 2020. The project aims to identify the sources and drivers of marine litter, improve monitoring tools, standardise the many ways in which observations of marine plastics are currently reported, and establish best practices, management measures and policy options. See www.cleansea-project.eu.

The 2014 Distinguished Guest Lecture "*Plastic debris in the ocean – solutions to a global environmental problem*" was given by **Richard Thompson** (Plymouth University), whose laboratory was one of the first to study marine plastic litter. Professor Thompson's particular interest in plastics began whilst volunteering to clean beaches of man-made debris. Although fishing crates, netting, tyres and other large plastic items washed up on the shoreline were easy to identify, collect and remove, the abundant smaller pieces of debris were often ignored. Seeing the challenge, Professor Thompson asked his students to find the smallest piece of plastic debris on a beach. They collected sand samples, examined them under a microscope and immediately saw brightly-coloured particles, some of which were smaller than the surrounding sand grains. These particles were subsequently identified as microscopic fragments of plastic: Professor Thompson coined the term "microplastics" in 2004 to describe them.

Some microplastics are emitted directly into the environment: for example, fragments of man-made fibres produced by washing clothes and polyethylene microbeads added to some shower gels are small enough to slip through the filters at sewage treatment plants. The rest derives from the breakdown of larger pieces of plastic. The burden of macroplastic items already floating in the ocean is such that, even if we could stop adding to the debris today, we would still face a legacy of many years of microplastic contamination. A wide-ranging study published by Professor Thompson's research group found microplastics in the inter-tidal sediments at every one of 18 sampling sites "representing six continents from the poles to the equator" [Browne *et al.*, *Environmental Science and Technology*, **45**, 9175, (2011)], suggesting that microplastic contamination is ubiquitous. The interaction of marine organisms with microplastics therefore occurs at the population level, and Professor Thompson's review of the various marine species found to have ingested plastics and their largely unknown toxicological effects echoed many of the points raised earlier by Dr Foekema and Dr Leslie.

Marine plastic litter has adverse economic and societal effects too. RNLI lifeboats are called out hundreds of times each year to assist mariners whose boats' propellers have become fouled by fishing ropes; holiday destinations spend money to keep their beaches pristine and attractive to the tourist trade. Professor Thompson is seeking to persuade fishermen to bring back to shore items of plastic debris they find at sea; readily accessible disposal facilities on the quayside encourage this effort and reduce any temptation to jettison unwanted/broken items at sea. These efforts have the added benefit of raising awareness amongst fishermen about how they engage with their environment. More widely, it is also important to generate public engagement. For example, images of large marine animals – a dead turtle entangled in a discarded fishing net or a seal struggling with a mooring rope around its neck – employ a shock factor that can be used to challenge the public to consider their role in limiting plastic debris.

Professor Thompson himself advocates the use of plastics, firmly believing that their value in transport, food preservation, electronic devices (the internet would be impossible without plastics), electricity transmission and renewable energy applications reduce our carbon footprint relative to the non-plastic alternatives. And as Professor Billingham opined in his opening talk, the chemist's greatest contribution to human health was the invention of plastics to construct clean water pipes and sewer pipes. As a society, we do, however, need to change the way we engage with plastics. For 50+ years we have been "trained" to view plastics as single use items; this is particularly true of plastic packaging material. Nowadays, there are opportunities to recycle (some) plastics, but product designers need to do much more to develop packaging that, in addition to looking attractive on the supermarket shelf, facilitates recycling after use. More also needs to be done to improve waste management facilities in developing countries to prevent plastics entering the environment because, once in the ocean, plastics debris from just one country may wash up on shorelines all over the world. UN Sustainable Development Goals will include "eliminating the pollution and dumping of toxic materials in water bodies, and protecting aquifers", which may help to guide governance of this problem – see http://sustainabledevelopment.un.org/focussdgs.html.

For Professor Thompson, the bottom line is that plastic debris is entering the oceans faster than we can possibly hope to remove it. The only solution, therefore, is to limit the emission sources of plastics into the environment through a combination of education, infrastructure changes and more intelligent designs for plastic items that address their full production/use/reuse life cycles.

The ECG acknowledges funding for this event from the RSC's Environment Sustainability and Energy Division (ESED).

The presentation to Dr Leo Salter (left) by the current Chair of the ECG, James Lymer (right), during the 2014 ECG AGM. Photographed at the Chemistry Centre, Burlington House.

The ECG's Annual General Meeting took place during the mid-meeting interval. In addition to the regular business of receiving the Chair's report on activities during the year, receiving the financial report and electing committee members, Leo Salter was presented with a commemorative plate bearing the RSC's crest in gratitude for his long service to the ECG. Leo retired from the ECG committee at the AGM, having previously been the ECG's Chair, Vice-Chair and the convener of many Distinguished Guest Lecture symposia. It was noted during the presentation that Leo's service to the ECG "is measured in decades, not years."

The authors are both committee members of the ECG.

Article

Plastic debris in the ocean – a global environmental problem

Richard Thompson: School of Marine Science and Engineering, Plymouth

Plastic marine debris is increasingly recognized as a global problem that requires urgent solution. Plastic debris is unsightly, hazardous to marine species as well as mariners, and has negative effects on the economy. The main solutions lie in reusing and recycling plastics and ensuring proper disposal of the remaining plastics.

Globally, over 280 million tonnes of plastic are produced annually. A key benefit of plastics is their durability, yet around one third of production is of disposable packaging, discarded within a year of production. As a result, plastic debris are accumulating in the environment as well as in regulated landfills (1). In the marine environment, 75% of all debris is plastic, contaminating habitats from the polar regions to the equator and from shorelines to the deep sea (2). The distribution of debris is not uniform, and it can be transported to locations far from population centres (3). This debris can persist for decades, but patterns of abundance over time are far from clear; some studies show an increase while others show no clear trend. It has been suggested that there may be unrecognised "sinks" where considerable quantities of plastic are accumulating (2).

Plastic debris is unsightly, has negative effects on the economy, and can present a hazard to mariners (4). Considerable expense is therefore invested in removing debris form ports and shorelines (5). Encounters between marine debris and marine species have been reported for over 660 species; 80% of these encounters are with plastic debris. Physical harm to individuals includes entanglement, leading to lacerations and mortality. For species like the northern fulmar, the majority of some populations (>95% of individuals examined) have plastic in their digestive tract (6). There is no evidence of population level consequences; it is very difficult, however, to link population level changes to single causative agents, and a lack of evidence does not necessarily imply a lack of effect.

In addition to physical effects, there are concerns that ingestion of plastic debris could lead to toxicological harm either because they accumulate persistent contaminants from sea water, or because they release chemicals incorporated during manufacture (such as plasticisers, flame retardants, and antimicrobials). Polyethylene and other plastics absorb persistent organic pollutants form seawater, and these can become orders of magnitude more concentrated than in the surrounding water (7). These chemicals can then be released in the gut, where desorption is facilitated by surfactants (8). Mathematical modelling indicates that the role of plastics in the transport of contaminates to organism may be relatively small compared to other pathways (9, 10); however, simple modelling approaches may be inaccurate because a range of factors such as pH and temperature will influence the equilibrium of chemicals between seawater, plastic and the tissues in an organism. For example, a warm blooded animal would have a greater potential to receive contaminants from plastic than a cold blooded organism. Further work to establish the relative importance of plastics as a vector under differing environmental and physiological conditions and in relation to uptake *via* other pathways including feeding and respiration is required to more fully understand the potential for plastics to transport chemicals to organisms.

With respect to the impacts of plastic in the environment, there are three important additional considerations. First, about 8% of world oil production is used to make plastic items, yet around a third of these items are discarded within a short time frame. Recycling end-of-life plastic can reduce the accumulation of debris while at the same time reducing the demand for fossil carbon (4). Secondly, the benefits from plastic items can be obtained without end-of-life plastics accumulating as debris in the oceans. Thirdly, discussions with other scientists, representatives from industry, policy makers and NGOs have shown that while there may be discussion and sometimes disagreement about the relative importance of the various impacts, there is typically universal consensus to reduce inputs of debris to the ocean.

Thus, marine debris is damaging to the economy, wildlife, and the environment, it is wasteful and unnecessary, and there is wide agreement that marine debris input needs to stop. What are the problems that retard progress? In my opinion the problems that hold back progress relate to prioritising solutions. Who should take action and, if there are costs, who should pay? The solutions principally lie on land rather than at sea and in decreasing order of merit are as follows:

1. Reduced material usage will reduce the quantity of end-of-life material that results;
2. Reuse of items will reduce the need for new plastic items and thus the quantity of end-of-life material;
3. Proper disposal of end-of-life items, ideally through recycling, will reduce the amount of waste reaching the ocean;
4. Recycling will reduce the accumulation of waste and simultaneously reduce demand for fossil carbon;
5. Energy recovery *via* incineration for items that cannot easily be re-used or recycled should be a last resort.

This hierarchy of options should be considered for every plastic product at the design stage to reduce both the use of fossil carbon and the accumulation of waste. Such principles are gaining momentum, for example, in the EU. Public interest can also lead to response from industry; some UK supermarkets have voluntarily opted to reduce use of single-use bags. However, some actions, if used inappropriately, could work against these goals. For example, use of bio-based carbon from agriculture is seen as a sustainable alternative to fossil carbon, but altering the carbon source does not reduce marine debris. Similarly, designing plastic products to degrade or disintegrate more rapidly can compromise the potential for product re-use, contaminate recycling, and lead to rapid accumulation of fragments in the environment (4). Policy-led coordination, supported by sound science, is needed to use the above measures for achieving change through a range of measures, including voluntary actions, incentives, taxes, and education (1). In particular there is a need to re-educate: during my life time, production of disposable short term products and packaging has rapidly increased, as has that of durable goods that cannot be repaired or renewed. In a growing culture of throw-away living, there is an urgent need to recognise there is no such place as "away".

This article is based on the author's 2014 ECG Distinguished Guest Lecture and on his contribution to 'The challenge: Plastics in the marine environment' in *Environmental Toxicology and Chemistry*, **33**, 5-10, (2014).

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Article

Polymers and their environmental degradation

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Plastics degrade after some time in the environment through hydrolysis or oxidation, making them weak and brittle. Full bioassimilation takes much longer, particularly in the ocean. Biodegradable polymers require industrial composting conditions to degrade fully. It is difficult to make materials with useful properties that degrade under less extreme conditions.

The modern world is unimaginable without polymers, one of chemistry's greatest contributions to human welfare. Thermosets like phenolic resins, which are crosslinked to the point of being essentially single molecules, are extremely durable and are used most in long-lived products. Less crosslinked polymers with mobile chains form rubbers, usually highly formulated mixtures loaded with carbon black and additives. However, the largest volume products are thermoplastics, typically linear chain polymers that soften on heating and can be processed into films, fibres, and bulk products.

Plastics consume waste products of the petroleum industry. In typical packaging applications, they save energy, waste, and emissions compared with alternatives. Current estimates put annual world production of plastics at over 250 million tonnes (1). The "big six" in market share – polyethylene (PE) (**Figure 1**), polypropylene (PP), poly(vinyl chloride) (PVC), polystyrene (PS), poly(ethylene terephthalate) (PET), and polyurethanes (PU) – account for around 80% of the demand for plastics in Europe.

Polymer properties are temperature-dependent because a ductile response to stress depends on the chains being able to change conformation fast enough for stress reduction without brittle fracture. An important parameter is the glass-transition temperature, above which long-range cooperative motions allow the polymer to flow. Most hard polymers have a glass transition temperature between 80 and 200 °C to minimise creep at room temperature while allowing processing without degradation.

PVC and PS are glassy and amorphous, with chains having no packing order. At room temperature, both are rigid and brittle. They and PU are mainly used in long-term applications, particularly construction and insulation. In contrast, PE, PP, and PET are semi-crystalline, with about 50% of the polymer being regularly packed in small crystals, while the rest is amorphous. These interlocking crystalline and amorphous regions stiffen and toughen the polymer at temperatures between the glass transition and the melting point. If the amorphous component has a glass transition well below room temperature (as is the case for PE), the material is extremely tough, whereas a higher glass transition improves strength and stiffness (as for PP and PET). PE, PP, and PET are extensively used in short-life applications, particularly packaging.

The first industrial polymers were modified natural materials, notably natural rubber and celluloses. Modern plastics are mostly derived from oil, although they represent only about 4.5% of oil consumption. Oil fractions can be converted into acids, amines, etc. and reacted to give step-reaction polymers, with functional groups (such as ester, amide, or urethane) in the main chain. In contrast, polymerisation of olefins and vinyl monomers gives full-carbon backbones. There is growing interest in polymers derived from biomass, whether synthesised *in vivo* [such as poly(hydroxy alkanoate)s from bacterial fermentation] or from bio-derived monomers (such as polylactide from cornstarch-derived monomers). Although growing, bio-plastics are still a tiny fraction of the market.

It is a myth that plastics are indefinitely stable in the environment. They get their mechanical properties from their very long, entangled, and perhaps crystalline chains, and even small levels of chain scission can destroy the toughness of a plastic, especially the semi-crystalline materials that rely on "tie" molecules to transfer load between amorphous and crystalline phases. Many polymers are unusable without additives to inhibit degradation. In common packaging materials, these additives are usually low-molecular-weight substances that interfere with degradation in many ways. They are consumed chemically and eventually stop protecting the polymer, which then degrades.

Thus, plastics are not simple. The polymer often contain several additives, which may be there to improve the product, provide colour, aid in manufacture, prolong its life, or protect it from extremes, such as fire. In use or storage, the formulation will be exposed to a wide range of degradative influences, including oxygen and perhaps elevated temperatures, contacting liquids, sunlight, and atmospheric pollutants. Failure usually takes one of two forms: *either* the material starts to lose its surface appearance by discoloration, loss of gloss, or the formation of white deposits, *or* it cracks and breaks.

Loss of toughness due to chain scission at ambient temperatures might be expected to occur by either hydrolysis or oxidation. Polymers such as polyesters that contain main-chain functional groups have potential for hydrolytic cleavage and might be expected to lose molecular weight in aqueous environments. Hydrolytic cleavage is, however, extremely limited in polymers like nylons and PET, because polymers are hydrophobic and the high glass transition temperature restricts chain mobility. By far the dominant mechanism of degradation of common plastics and rubbers is oxidation.

Polymer oxidation is an autoaccelerating free-radical process that involves the formation and decomposition of hydroperoxide intermediates. It is accelerated by heat, light, and contact with transition metals. Reactions of the intermediate free radicals cause chain scission and produce polar products, including esters, ketones, alcohols and acids. Unlike hydrolysis, oxidation can be slowed (or accelerated) by small amounts of additives, and antioxidants are typically added to common thermoplastics at low (<0.1 wt%) concentrations.

Although small amounts of chain scission in a plastic can produce a weak, brittle material, full bioassimilation is much slower. It requires the entangled chains to be cleaved to fragments that are small enough for assimilation, which requires a hydrophilic surface and functional groups that are attacked by water and enzymes. Polyesters are the most commonly used synthetic polymers that can biodegrade hydrolytically. However, there is a trade-off between biodegradability and physical properties. It is possible to make polymers that bioassimilate in less than a year in industrial composting at >50 °C, but it is extremely difficult to make products with useful properties that biodegrade significantly under less extreme conditions, for example in home composting.

Carbon chain polymers are highly resistant to hydrolysis because they have no sensitive sites in the main chain and are hydrophobic. Once oxidised to low molecular weights, the polyolefins do become hydrophilic and biodegradable, but the time scales for completing the whole oxidation and bioassimilation process are extremely long unless pro-oxidant additives are used.

It is particularly difficult for degradation of plastics to occur in the sea, although there is very little data on marine degradation. Hydrolysis is too slow at typical sea temperatures. Although solar near-ultraviolet light accelerates environmental degradation of most plastics, a crucial part of the acceleration is due to solar heating. The sea acts as an effective coolant, and a plastic that loses its properties rapidly in land solar exposure may last a great deal longer when floating in seawater.

This article is based on the author's talk at the 2014 ECG Distinguished Guest Lecture & Symposium.

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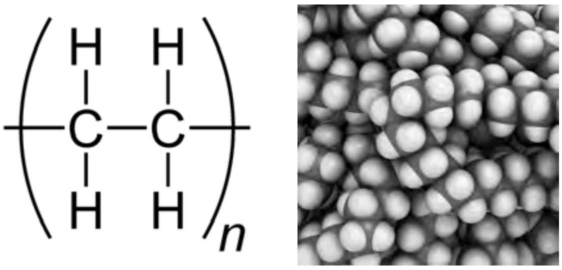

Figure 1. ***Plastic good, plastic bad.*** *Polyethylene is one of the "big six" plastics in terms of market share. It is often used in packaging but deteriorates only slowly in the environment. Structural formula (left}; space filling diagram (right). Image credit: Shutterstock*

Article

150th anniversary of the establishment of the Alkali Inspectorate

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The Alkali Inspectorate was established on 1 January 1864 following parliament's approval of the Alkali Act (1863) in July 1863. The Inspectorate aimed to control the release of damaging acid gas (hydrogen chloride) from alkali works. The legislation signified a sea change from the existing laissez faire approach to industry.

Robert Angus Smith* (1817–1884). *Reproduced courtesy of the Library of the Royal Society of Chemistry.

By the 1850s, some 250,000 tons of salt were being decomposed annually in alkali works in the UK, resulting in the release of about 115,000 tons of acid gas. Legal proceedings against these works were largely unsuccessful, because it was difficult to attribute damage from the gas to a particular work and to conclusively attribute any damage to acid gas. Serious lobbying began only when the landed gentry and wealthy landowners experienced reductions in their land values and extensive damage to their woodlands. In 1862, the House of Lords set up the Select Committee on Injury from Noxious Vapours, with Lord Derby as chairman. *Punch* referred to the Select Committee as 'Derby's Smells Committee' (1). During the Select Committee hearings, William Gossage, an alkali manufacturer in Worcestershire, gave details of his acid tower invention in 1836 that could condense the acid gas almost completely. This invention formed the basis of the Alkali Act (1863), with the Inspectorate established to ensure that the condensation limit of 95% was met by all Leblanc alkali works. The Board of Trade, as the responsible government department, appointed Robert Angus Smith as the first Inspector and gave him a blank slate as to how the Inspectorate should monitor the operation of the works to ensure that the condensation limit was achieved.

Monitoring procedures

After a tussle with the Treasury, the Board of Trade was allowed to appoint four sub-inspectors (one for each of the four regions into which Britain was divided) to work alongside Angus Smith. The next stage was to draw up procedures that were consistent and scientific, because the information might form evidence in a court of law should a prosecution prove necessary. Angus Smith tried to avoid such prosecutions wherever possible because of his experience as an expert witness in the Spence court case of 1857 (2).

Angus Smith was adamant that analytical chemistry had to be at the core of the procedures if an objective assessment was to be made on whether an alkali works met the minimum condensation limit. When inspections got under way, another difficulty arose. With the large number of alkali works and the small number of inspectors, each works was only visited intermittently, providing works with opportunities to release acid gas undetected. To combat these digressions, Alfred Fletcher, one of the first sub-inspectors (who took over as Inspector when Angus Smith died in service in 1884), developed the compound self-acting aspirator, which could take samples of air in the flues leading to the chimney over a number of days. These aspirators were placed permanently in the flues and were sealed so that no one could interfere with their operation (3).

Inspectors as peripatetic consultants

Another major challenge for Angus Smith and his inspection team was to develop cooperative relations with the alkali manufacturers, because inspection required access to the works and working plant. During the Select Committee hearings in 1862, manufacturers expressed alarm about government interference in the workings of industry. John Hutchinson, an alkali manufacturer in Widnes, speaking on behalf of some manufacturers, submitted a statement of cooperation. Nevertheless, when inspections got under way there was often an uneasy relationship, and Angus Smith knew he had to win over all manufacturers if the condensation limit was to be met.

Alkali works were not always operated in an effective way that allowed them to meet the limit. Few works had qualified chemists; most proprietors were unqualified entrepreneurs, and processes were carried out in a rote manner using a recipe-type approach. The inspectors found themselves advising manufacturers on the operation of their plant and thereby acting as peripatetic consultants. This was potentially dangerous because the inspectors might be accused of giving one business a commercial advantage over another. The inspector had to focus on achieving the condensation limit.

Another manifestation of this commercial sensitivity was the handling of information gathered about each works during inspections. Angus Smith had to produce an annual report for Parliament on the workings of the legislation. His reports contain a considerable amount of technical information, much of which could be deemed commercially sensitive. The information is listed against a works registration number. The original register is held today by the Environment Agency, and, if the number of a particular works is known, it can unlock a large amount of information about the scale and operation of the works. The manufacturers eventually cooperated when it became clear that meeting the minimum limit enabled them to avoid legal challenge by the Inspectorate or by other parties.

Further legislation

The original 1863 legislation was approved for an initial five-year period; in 1868 it was approved indefinitely. Subsequent changes to the terms of the legislation aimed either to make it operate more effectively or to go beyond the alkali industry to include other chemicals and processes. An Amendment Act in 1874 replaced the difficult-to-assess percentage measure with a volumetric measure: “each cubic foot [28 litres] of air escaping into the atmosphere there is not to contained more than one-fifth part of a grain [0.013 g] of muriatic acid” (4).

The Royal Commission on Noxious Vapours (1876) began a discussion on another important principle for the Inspectorate, namely adoption of the “best practicable means” in controlling a polluting gas. Angus Smith and Alfred Fletcher were adamant that it was no good waiting for the final technical solution but that manufacturers should always make every effort to meet the limit. This would ensure that manufacturers at least attempted to meet the limit; when a better solution arrived, all works could adopt it. Such an approach put an onus on the manufacturers, who by this time had begun to employ qualified chemists to provide the expertise to improve plant rather than relying on the Inspectorate. This principle was incorporated into the Alkali Act (1881) and remains a backbone to pollution control.

The responsibilities of the Inspectorate increased steadily through the 20th century. By 1956 the Inspectorate was responsible for 1,794 processes in 92 works in England and Wales, and for 116 processes in 82 works in Scotland. As W. A. Damon (Chief Inspector from 1929 to 1955) reported in 1956, concerns were still being raised over a number of industries, including sulphuric acid, viscose processes, cement works, coal carbonization works, steel works, and ceramic works (5). As the scale of industrial development grew and chemicals became ever more sophisticated, the vigilance of the Inspectorate has helped to protect air quality in Britain. The Inspectorate has served Britain well during the last 150 years. Today, as HM Inspectorate of Pollution within the Environment Agency, it continues this important role.

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Article

Raising air quality awareness among school children and the public

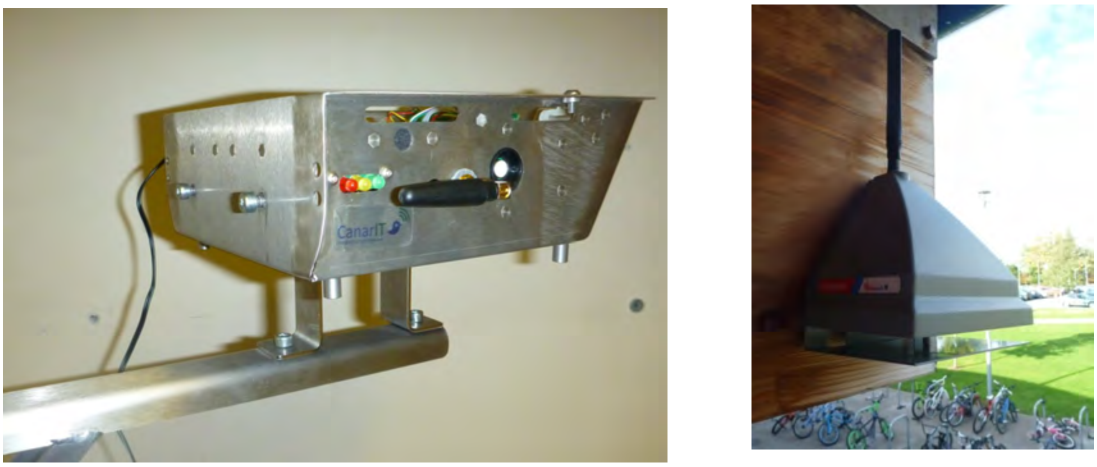
**Zoë Fleming: National Centre for Atmospheric Science,
University of Leicester**

A new initiative to set up mobile atmospheric chemistry instruments in schools has been funded by the RSC. Using low-cost sensors that can measure nitrogen oxides, ozone, and total organics, the initiative allows school children to become involved in the monitoring of pollution in the air around them.

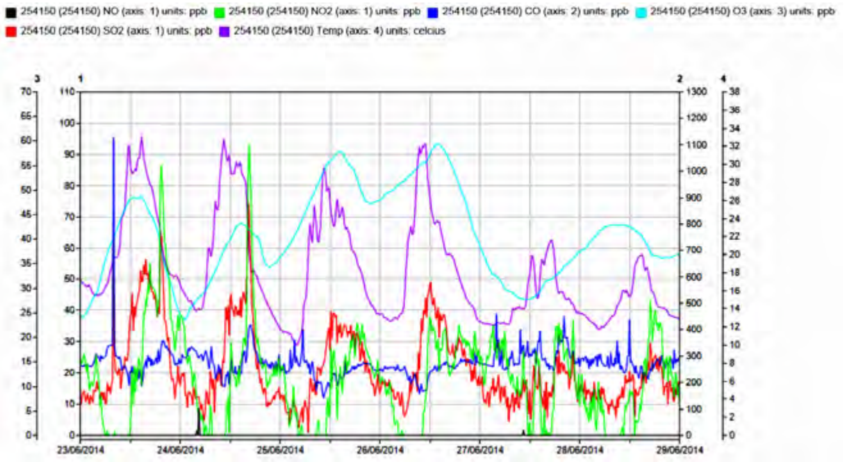
A new type of air quality monitoring instrumentation is emerging on the market, allowing small mobile sensors to track air pollution in any location. The Environmental Chemistry group of the RSC received funding to start up an Atmospheric Chemistry educational toolkit for use in schools across the country. We set up at Bushloe High school in Wigston, Leicester, for a few weeks in October 2013 and also demonstrated to school children in Leicester at the Abbey Road Pumping Station Museum.

Since then, the instruments have been measuring at a busy traffic junction, in a concerned Leicester resident's garden, and at the city council air quality monitoring station run by Leicester University. The instruments have been characterised and calibrated, and have proved to be consistent, allowing the data to be used for both real-time atmospheric chemistry research and for public and school outreach projects. We teamed up with Leicester city council and the JOAQUIN European air quality project in April to run a big outreach event in Leicester city centre to educate the public about air quality. By coincidence, the event was held during the week when Saharan dust and high air pollution were all over the news, and many concerned members of the public approached us to find out more.

We have created posters and activities about atmospheric chemistry and air pollution for children of all ages to learn from, including a data analysis tutorial for children from about 10 years old to A-levels. Science classes at schools where the instruments are temporarily based can go through an analysis and interpretation of the air pollution at their school. Thanks to more RSC funding, we are due to extend the project to more local schools in autumn 2014 and make it a regular activity,



The AQMesh instrument (left) is battery powered and thus very mobile and adaptable. It measures O_3*, NO,* NO_2*, CO ,* SO_2*, temperature and humidity. The CanarIT™ (right) needs to be plugged into the mains. It measures* O_3*,* NO_2*, Total Volatile Organic Compounds (T VOC), dust, noise, temperature and humidity. Both instruments stream data continuously to a web interface for graphical data display or to download data for analysis. A small meteorological station stationed next to the sensors with the interface screen indoors adds another level of analysis.*



Live data from the AQMesh web site, used to input the school's pollution data into a case.

School outreach activities carried out to showcase the instruments and atmospheric chemistry and air pollution in general.

moving the instruments from school to school every few weeks so that they can compare their data with other local schools. For schools awaiting the instruments or any other interested school, we have produced a tutorial to interpret air pollution in their local area using public data from the DEFRA air quality web pages through the AURN (Automatic Urban and Rural Network). The schools access the nearest air quality station and extract data from the last week's time series plot, pulling out minimums and maximums for weekdays and weekends, at midday and at the morning rush hour. These values are tabulated into spreadsheets that we and the school children collate to create a local picture of pollution. Our ambition is to create a web site that enables schools around the country to add their spreadsheet online to create a map of pollution levels across the country.

These activities not only hone the pupils' scientific observation and data interpretation skills, but show them how this science fits into their daily lives, how it could affect their health, and also how air quality is intimately linked to human activities and car usage. We hope to start a dialogue between the children, their parents, and the community about the air quality in their region and at the same time inspire the next generation of environmentally-aware scientists.

Getting involved

Please contact Zoë Fleming (zf5@le.ac.uk) if you want to suggest a host school for the project or would like to get involved in the project. See also a related article in The ECG *Bulletin*, February 2013, pp 19-21.

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The author is an ECG committee Member.

Book review

Robert Angus Smith and the origins of the environmental chemist

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With increasing levels of industrialisation and awareness of pollution in nineteenth-century Britain, new competencies were needed over a relatively short period of time to fulfil the demands by legislators, industrialists, and the general public for knowledge in this field. In his newly-published book published by Ashgate, *Acid Rain and the Rise of the Environmental Chemist in Nineteenth -Century Britain: The Life and Work of Robert Angus Smith*, Peter Reed brings the rise of the environmental chemist during this period to life. The book forms part of Ashgate Publishing's Science, Technology and Culture, 1700-1945 series.

Rather than providing a comprehensive account of the role and influence of environmental chemists in the 1800s, the author focuses on the role of environmental chemist Robert Angus Smith. Although not widely recognised nowadays, Smith had a notable impact on the field and played an important role in the rise of the environmental chemist. At key instances, the author recounts the wider context in which Angus Smith was operating, particularly in relation to the British chemical industries and environmental movements.

The book starts with a biography of Robert Angus Smith from his early days in Scotland to his death from complications related to pernicious anaemia in 1884. Subsequent chapter focus on such topics as the influence of other scientists on his career; how his life in Manchester in the mid-1800s shaped his interest in sanitation, air and water quality; and the increasing role of civil scientists in society. A limitation of the way the author has shaped the book is that particular aspects of his life are discussed repeatedly over a number of chapters. The final chapters give an overview of Angus Smith's legacy; an extensive bibliography of his manuscripts, books, reports, and journal articles; and a bibliography of key texts on Angus Smith and environmental chemists in nineteenth-century Britain.

At the start of his career, Smith's interaction with other leading scientists of the period, namely Thomas Graham, Justus von Liebig and Lyon Playfair, had a crucial impact on his interests. After moving to Manchester in the mid-1800s, he acquired first-hand experience of a city undergoing increasing industrialisation and the associated reduction in environmental quality and sanitation, largely as a result of sub-standard housing, inadequate fresh water and coal burning.

As his public and professional profile rose, Smith became increasingly sought after in matters related to air and water quality, sanitation, and disinfection within Britain. After he had reviewed the operation of an alum manufacturer, Smith was requested to testify in court proceedings initiated against the manufacturer. This experience enabled him to excel further in his later role as an inspector with the Alkali Inspectorate, which was key to changing British regulatory frameworks to safeguard the environment and human health (see this issue, pp 16-17). Improving manufacturing operations included acid tower improvements and better means of sampling and analysing air quality to allow for objective assessments. New regulations were also implemented, elements of which remain in place today, such as the requirement to implement the "best practicable means."

The focus on the life and works of a single individual makes the book accessible to a reader not looking for an academic text on the history of environmental chemists, but aiming to obtain a better understanding of the history of environmental chemistry. Those interested in more information will find the suggestions for further reading and citations to relevant texts helpful. A wide range of readers should find this book a useful and interesting read.

Forthcoming meeting

New developments in the analysis of complex environmental matrices

Hosted by the ECG at the Royal Society of Chemistry, Burlington House, London, Friday 6 February 2015.
Following the success of 'Recent advances in the analysis of complex environmental matrices' held in 2013, (reported in the ECG *Bulletin*, July 2013, pp 5-9), this new meeting aims to cover the development in analytical instrumentation that makes it possible to simultaneously analyse numerous pollutants in complex environmental matrices with minimal sample clean-up.

For further details visit http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/

ECG Environmental Briefs

Asbestos in soils (ECGEB No 5)

James Lymer (Wardell-Armstrong)

The UK along with other industrialised nations has a legacy of land that is contaminated with materials from previous use or from naturally occurring sources. This Environmental Brief outlines asbestos in soil, the risks and assessment methodologies available.

In the UK, asbestos was extensively used in buildings and other products in the 20th century. In 1970, strict regulations were introduced to regulate the use of asbestos in the workplace and to limit employees' exposure to it. There are three main mineral types: amosite (brown) and crocidolite (blue), use of which was banned in 1985, and chrysotile (white), use of which was banned in 1999 in the UK.

Chrysotile, white asbestos, empirical formula $Mg_3(Si_2O_5)(OH)_4$. Image credit: Shutterstock

There is a background concentration of airborne asbestos fibres in the environment due to historic usage and waste disposal. Asbestos in buildings is strictly regulated in the UK (e.g. through the Control of Asbestos Regulations 2012) with surveys, registers and removal methodologies. In contrast, the presence of asbestos in soil is usually only discovered during site investigation work prior to redevelopment of a site or if the site is deemed potentially "Contaminated Land".

Asbestos can be present in the environment as free fibres or bound in a matrix as an asbestos-containing material (ACM). Naturally-occurring asbestos is not commonly found in UK soils; it is therefore most likely that manmade ground (such as ash, demolition materials, and spoil) is the primary source, and it is likely to be commonplace within the soil matrix at brownfield sites. Asbestos usually occurs discretely in an impacted area and will not undergo biodegradation over time to form less harmful materials (i.e. it is very persistent), although ACMs can be physically degraded over time. It can migrate through physical disturbance, resulting in possible release of its dangerous fibres.

Asbestos toxicology mainly affects humans rather than being a risk to the environment. Asbestos fibres that are not in the air cannot be inhaled and hence do not pose a significant risk to health until they become airborne, can be inhaled, and are retained in the lungs. Inhalation of asbestos fibres can produce a range of lung-associated diseases, including asbestosis, lung cancer, and mesothelioma. The latter two diseases are considered to be the primary diseases of concern at asbestos exposure levels in the environment.

Assessment methodologies

UK: Asbestos on contaminated sites, ICRCL, 1990

This guidance was published in 1990 in the UK by ICRCL (1) based on contemporary research; it reported that soils containing as little as 0.001% free asbestos fibres could liberate significant airborne free fibre concentrations. Although 0.001% has been considered a screening value by some risk assessment practitioners since the 1990s, recent guidance by CIRIA (C733) on asbestos in soil indicates that 0.001% is not a level below which ICRCL considered risks to be acceptable.

UK: Asbestos in soil and made ground (C733), 2014

In March 2014, UK guidance on asbestos in soil was published by CIRIA (2). This guidance has stated that screening values for asbestos in soil such as 0.1% and 0.001% should not be used in the UK and that an appropriate generic screening value cannot be derived at present without a policy decision because of the limited understanding of the soil-to-air fibre release relationship for asbestos. The risk assessment for asbestos is a function of the composition and quantity of fibres released from the soil, the exposure scenario, and the critical receptor. The CIRIA guidance has proposed adopting exposure risk assessment models that predict the lung cancer and mesothelioma risks associated with exposure to airborne asbestos.

Netherlands: RIVM (2003)

Dutch intervention values (3, 4) are used as generic soil standards (Tier 0) to trigger remediation. A tiered approach to assess the risk from asbestos in soil considers site specific circumstances at each tier, with less conservatism relative to the previous tier. An intervention value for asbestos was derived at 0.01% w/w fibre equivalents for friable and bound asbestos, and 0.1% w/w fibre equivalents for bound asbestos assessed to be in "good condition" (not seriously weathered or eroded).

Australia: Guidelines on the assessment, remediation and management of asbestos contaminated sites in Western Australia, May 2009

In 2009, guideline values for asbestos-containing materials in soils were derived for the following categories (5): asbestos-containing material (ACM – non-friable matrix material); fibrous asbestos (FA – friable and fibrous material); and asbestos fines (AF – sub-7mm material including free fibre).

The guideline values are as follows:

- 0.001% weight for weight (w/w) asbestos for FA and AF (all site uses)
- 0.01% w/w asbestos for ACM (residential use, childcare centres etc.)
- 0.04 % w/w asbestos for ACM (residential, minimal soil access, e.g. residences having fully and permanently paved yard space)
- 0.02% w/w asbestos for ACM (parks, public open spaces, playing fields etc.)
- 0.05 % w/w asbestos for ACM (commercial and industrial sites).

These criteria can be used as soil clean-up goals, or site-specific goals can be developed. Asbestos buried deeper than 3 metres below ground level is not usually regarded as contamination provided it is not likely to be disturbed.

The examples from the Netherlands and Australia show that generic screening values are available overseas. However, UK practitioners and regulators of contaminated land are left in a situation where there is an increased awareness of asbestos-related risk and liability on sites, yet there are no authoritative UK-generic screening values for asbestos in soil.

Remediation

If asbestos in soil presents a potentially unacceptable risk to human health, the most likely remediation strategy is to remove the ACMs that are present or encountered during remediation, although these works may inadvertently expose workers and/or members of the public to asbestos fibres through disturbance. The exposure of site workers during any excavation, storage, treatment, placement, or disposal of asbestos should be assessed and managed in accordance with the regulations. The damping down of soils before and during remediation can significantly reduce the release of airborne fibres.

Chemical, thermal and biological treatment techniques that are applicable to organic contaminants such as benzene are ineffective on asbestos as it does not burn; it is biologically inert and chemically unreactive. In the presence of contaminants other than asbestos, the likely preferred option will be one that mitigates both the risks from asbestos and from the other contaminants.

Where asbestos is the single or primary contaminant in soil, the remedial options include leaving the asbestos in-situ and undisturbed with or without a capping layer comprising uncontaminated soil; re-use of asbestos in soil; treatment of asbestos in soil e.g. separating asbestos pieces from the soil through hand-picking or solidification/stabilisation of the soil; or off-site waste disposal of asbestos in soil to a suitably licensed landfill.

Acronyms

ICRCL	Inter-Departmental Committee on the Redevelopment of Contaminated Land
CIRIA	Construction Industry Research And Information Association
ACM	Asbestos-containing material

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The author is Chair of the ECG.

ECG Environmental Briefs

Pourbaix (pE-pH) diagrams for the aquatic environment (ECGEB No 6)

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Pourbaix diagrams (or eh-pH, or pE-pH diagrams) can help environmental workers to "predict" the physical and oxidation state of a chemical element in different aquatic environments. Pourbaix diagrams can explain and predict behaviour of contaminants in the environment but they should be used with caution and knowledge of their weaknesses.

The release of a potentially harmful chemical into the aquatic environment requires knowledge about the chemical released and any subsequent transformation of the chemical. Redox and acid-base reactions within the aquatic environment may cause a change to the oxidation state, molecular formula and physical state of the elementand hence toxicity. A Pourbaix diagram (named after the Russian-born Belgian chemist Marcel Pourbaix) is a stability diagram (roughly similar to a phase diagram) and demonstrates which species predominates under different conditions of redox potential and pH. For example iron exists differently in the oxygen poor waters of ground water to that of acid mine drainage and that of an aerated stream.

Provided here is the briefest introduction to Pourbaix diagrams to show their potential use and common pitfalls. The author has found the use of Pourbaix diagrams useful in teaching and the explaining of concepts. Future *ECG Environmental Briefs* will show more advanced uses for the environmental professional, and an interested reader is referred to detailed texts, such as (1).

Introduction to the diagram

A Pourbaix diagram is typically electrode potential (relative to a standard hydrogen electrode potential) or pE plotted *versus* the pH of an aquatic media. pE is more common for environmental science and is similar to the definition of pH:

$$\mathrm{pH} = -\log a(\mathrm{H^+_{(aq)}})$$

i.e. the logarithm of the activity of the hydrogen ion, and

$$\mathrm{pE} = -\log a(\mathrm{e^-})$$

i.e. the logarithm of the hypothetical activity of electron.

Put simply, pE is a measure of the aquatic system to reduce or oxidise.

A typical Pourbaix diagrams for iron calculated using free software (2) is shown in **Figure 1**. The dashed lines bound the region where liquid water is stable; above the upper dashed line water is oxidised:

$$\mathrm{H_2O_{(l)}} \longrightarrow \mathrm{2H^+_{(aq)}} + \tfrac{1}{2}\,\mathrm{O_{2(g)}} + \mathrm{2e^-}$$

Below the lower dashed line water is reduced:

$$\mathrm{H_2O_{(l)}} + \mathrm{e^-} \longrightarrow \mathrm{OH^-_{(aq)}} + \tfrac{1}{2}\,\mathrm{H_{2(g)}}$$

The lines on the graph enclose regions where different forms of iron may predominate. The lines are drawn where the activities of two neighbouring species are equal. The activity of solids in a Pourbaix diagram are explained in (3). Vertical lines represent acid-base reactions and horizontal lines represent redox reactions.

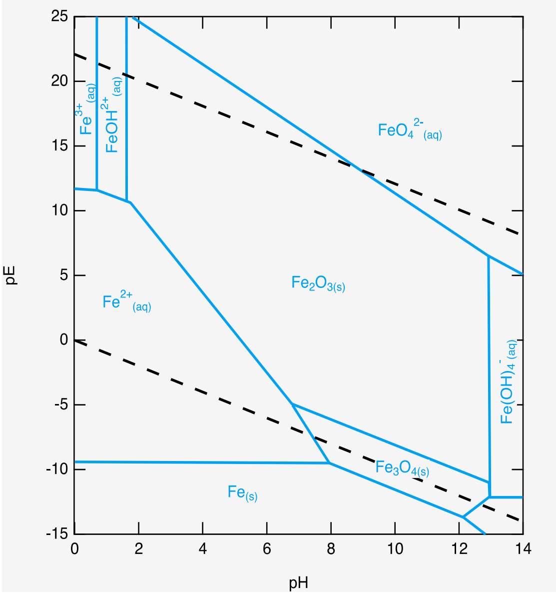

Figure 1*. Pourbaix diagram calculated for iron at 10 ° C and [$Fe^{3+}_{(aq)}$]$_{total}$=1 μM, using the Chemical Equilibration Diagram software (2). The graph is indicative and should not be considered accurate.*

Consideration of **Figure 1** shows that a ground water (e.g. pE<0 and pH~6.5–7.5) may contain iron as $Fe^{2+}_{(aq)}$, surface waters (e.g. pE>0 and pH ~6.5–7.5) will contain Iron as the solid Fe_2O_3 and extreme acid mine drainage water (pE>0 and pH<3) may contain Iron as $Fe^{3+}_{(aq)}$. pE-pH diagrams with typical values of pE and pH for natural water bodies can be found in Krauskopf and Bird (3) and Baird (4). These two sources have broadly similar diagrams but with some differences. It is difficult to measure the pE of natural waters as the water may not be at equilibrium or be in equilibrium with the probe measuring pE (5).

Figure 2 demonstrates that Pourbaix diagrams are very sensitive to the presence of other chemical species. Adding sulphur to previous system, **Figure 1**, demonstrates a new Pourbaix diagram, **Figure 2**, which may be used to explain the chemical speciation of iron occurring in natural waters containing sulphur or with a sulphur lithology.

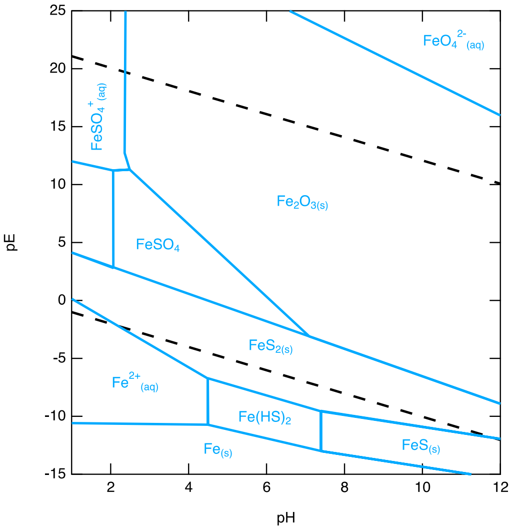

***Figure 2**. Pourbaix diagram calculated for iron at 10 °C with* $[Fe^{3+}_{(aq)}]_{total}=1\ \mu M$ *and* $[SO_4^{2-}{}_{(aq)}]_{total}=10\ mM$*, using the software in (2). The graph is indicative and should not be considered accurate.*

Important caveats

There are many considerations with the interpretation of Pourbaix diagrams. Three caveats with Pourbaix diagrams are:

1. The diagrams represent thermodynamic equilibrium. They do not indicate how quickly the system will come to equilibrium and a water body may effectively may never reach equilibrium. The kinetics of each situation must be assessed independently especially as many of the redox reactions are biologically mediated.
2. Pourbaix diagrams are constructed for the given conditions of temperature, pressure and activities of species present. Thus a general Pourbaix diagram is unlikely to be accurate for a specific situation.
3. Pourbaix diagrams display the dominating species. However, the systems are assumed to be at equilibrium thus other chemical species may be present at appreciable, but not dominant, concentrations.

Ideas for exploration or teaching

To further explore Pourbaix diagrams the chemical equilibrations software listed at the end of this article may be used to consider the following systems.

1. To complement a water quality field trip to Southern Florida looking at phosphate eutrophication of water bodies, students create Pourbaix diagrams of: (a) phosphorus, (b) phosphorus and aluminium, (c) phosphorus, aluminium, and iron, (d) phosphorus, aluminium, and calcium. With these diagrams they can explain why aqueous phosphate pollution can move through sandy soils to the water bodies.
2. Create Pourbaix diagrams for radionuclides of actinides, (a) with and without carbonate included, or (b) considering if artificial wetlands could be useful in trapping actinides from surface storm water from plants using radionuclides.

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