

ECG *Bulletin*

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This and previous issues of the ECG *Bulletin* are
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This is a report of a meeting jointly organised by the RSC Toxicology Group and

UK aquifers. Other emergent contaminants include

Alistair Boxall (University of York) gave a presentation *Side effects of medication in the soil environment*.

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* 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.

Robert Kalln (University of Strathclyde), in his talk on *Environmental forensics with GCxGC TOFMS analysis*

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

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

The atmospheric chemistry of forests, a forgotten molecule, and a football match

field measurements investigating volatile organic compound (VOC) emissions over the boreal forest in Hyttiala, 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

Measuring fluxes of biogenic volatile organic compounds above the Amazonian rainforest using PTR-MS

of characterising and working with long inlet lines. The meeting then took a slight change of emphasis, with **Professor Paul Thomas** (Loughborough University)

Does it have to be blood sweat and tears? Non-invasive approaches to therapeutic measurements, and emergency medicine

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

atmosphere

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-

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

MS approaches, and the use of novel ion chemistries to exploit or suppress impacts of secondary chemical interactions.

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 ECG Distinguished Guest Lecture and supporting talks link fundamental chemical science with a current environmental issue.

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

equilibria re-partition the POPs between the plastic and

-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)

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

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

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

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 from 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 from 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 contaminants 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

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,

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 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

additives are usually low-molecular-weight substances that interfere with degradation in many ways. They are consumed chemically and eventually stop protecting the

The Alkali Inspectorate was established on

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.

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 15,000 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 and to conclusively attribute any damage to acid gas. Serious lobbying began only when the *Manchester Guardian* and other wealthy individuals 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 Darby as chairman. It referred to the Select Committee as

Dug the hearings, William Gossage, an alkali

Select Committee

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

the atmosphere there is not to contained more than one-

The Royal Commission on Noxious Vapours (1876) began a discussion on another important principle for

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.

References

1. *Punch*, 24th May 1862, p 204.
2. Peter Reed, *Acid Rain and the Rise of the Environmental Chemist in Nineteenth-Century Britain: The Life and Work of Robert Angus Smith*, Ashgate Publishing, Farnham, UK, 2014, pp 85-91.
3. pollution 1823 *Transactions of the Newcomen Society*, **78**, (2008), pp 118-119.
4. *Alkali Act (1863) Amendment Act 1874*, P.P. 1874 (99).
5. *Annual Report of the Council. Royal Society of Health (Great Britain)*, **76**(9), (1956), pp 566-575.

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

moving the instruments from school to school every few

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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,



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

Pourbaix diagrams (or eh-pH, or pE-pH diagrams) can help environmental workers

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 element and 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:

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

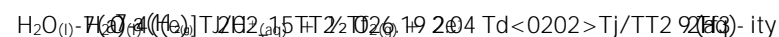
i.e. the logarithm of the activity of the hydrogen ion, and

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

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:



Below the lower dashed line water is reduced:

