

# Bulletin



**A crop duster flies low spraying farm fields. Credit: B. Brown/Shutterstock**

## In this issue

The impacts and regulation of pesticides and other chemicals were the focus of a joint RSC ECG–Toxicology Group meeting on *The Legacy of Rachel Carson* held in October 2012 to commemorate the 50th anniversary of the publication of *Silent Spring*. Reports of this meeting may be found on pp 4–9 of this issue. Elsewhere, Peter Reed (pp 22–26) and Kris Wadrop (pp 27–29) describe aspects of waste disposal, which reflect evolving societal

and legislative attitudes to the problem of ‘waste’ in the UK’s current post-industrial revolution landscape compared with its Victorian past. The disposal of waste from the Leblanc alkali industry in the 19<sup>th</sup> century affected the health of local populations and degraded the landscape. By contrast, the recycling of organic waste in the 21<sup>st</sup> century offers economic opportunities for the UK and will benefit the environment.

## Also

Other articles in this issue discuss field work and classroom demonstrations on the environment for young people (pp 19–21) and the challenges of turning science into policy (pp 17–18). Plus reports from a meeting on Soft Ionisation Mass Spectrometric Techniques and the abstracts from the latest ECG Atmospheric and Environmental Chemistry Forum, which took place at Leicester University last June.

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### Editorial team

#### Executive editor

**Julia Fahrenkamp-Uppenbrink**  
ecgbulletin@hotmail.co.uk

#### Commissioning editor

**Rupert Purchase**  
rp@rupertpurchase.demon.co.uk

#### Production editor

**Roger Reeve**  
University of Sunderland  
roger.reeve@sunderland.ac.uk

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## Environmental Chemistry Group

[www.rsc.org/ecg](http://www.rsc.org/ecg)

The RSC's Environmental Chemistry Group (ECG) considers all aspects of the complex relationships between chemistry and the environment. The ECG aims to understand the behaviour of chemical species in the water, soil and atmospheric environments; exploring their sources, reactions, transport and in particular their effects on each of these environments.

### Chair

Bill Bloss, University of Birmingham  
[w.j.bloss@bham.ac.uk](mailto:w.j.bloss@bham.ac.uk)

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[Rainscapper@hotmail.com](mailto:Rainscapper@hotmail.com)

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### Honorary Treasurer

Jo Barnes, University of the West of England, Bristol  
[annaoj\\_senrab@hotmail.com](mailto:annaoj_senrab@hotmail.com)

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# Chairman's report for 2012

During 2012, the Environmental Chemistry Group committee organised a number of successful meetings across a range of topics and formats – including some meetings in collaboration with other interest groups and organisations.

The first event of the year was our flagship **Distinguished Guest Lecture & Symposium 2012**, which addressed the topic of **Energy, Waste & Resources – three sides of the same coin?** Three presentations preceded the DGL, which was delivered by Professor Paul Williams (Leeds University) with the title “Fuel, Chemicals and Materials from Waste”.

In June, the third **Atmospheric and Environmental Chemistry Forum** for PhD students and early career researchers was held, this time at the University of Leicester. The meeting included poster and oral presentations in an informal environment, followed by a careers discussion with a small panel covering academic, industry and consultancy pathways. For abstracts from this meeting, please see pp 30-38 of this edition of the ECG *Bulletin*.

Throughout the year, the ECG has participated in the **RSC £1000 challenge**, through which the RSC provided a £1000 budget to interest groups to devise their own activity to promote chemistry (very loosely defined). Zoë Fleming from Leicester University led the development of a series of simple environmental sampling experiments for school (KS3) and university students. The experiments were trialled by young people aged 16-19 on a British Exploring expedition to Norway during the summer (see pp 19-21), and will be introduced into local schools in the near future. There is scope to extend this and related activities in the future, with funding provided by the RSC.

ECG members with ideas and/or interest in this are encouraged to get in contact.

In the autumn of 2012, the ECG and the RSC Toxicology Group jointly organised a meeting on **The Legacy of Rachel Carson – 50th Anniversary of Silent Spring**. The meeting explored the issues raised in the book, the eventual ensuing political action (and controversy), and our present-day understanding of the environmental chemistry of persistent organic pollutants and their toxicology. For reports from this meeting see pp 4-9.

This was followed in November by a half-day meeting on **Soft Ionisation Techniques in the Environmental Sciences**, organised jointly with the Mass Spectrometry Group of the Institute of Physics and held at the University of Birmingham. A series of invited speakers gave in-depth presentations around the subject of new ionisation approaches and their applications. Following on from the meeting, it is intended to form an informal user group in this area (see the meeting report on pp 13-14).

Alongside our programme of events, four members of our committee, stalwarts Rupert Purchase and Roger Reeve, and new editorial team Julia Fahrenkamp-Uppenbrink and Aleksandar Radu, are producing the biannual **ECG Bulletin**. With the transition to electronic publication, future issues should include more dynamic content and hyperlinked material.

In the first quarter of 2013, the ECG is linking up with the Separation Science Group of the RSC Analytical Division to host a substantial event on the **Analysis of Complex Environmental Matrices** (scheduled for Thursday 28<sup>th</sup> February 2013 at the RSC, Burlington

House, London; see details on pp 15-16). Then, in March, this year's **ECG Distinguished Guest Lecture & Symposium** will be given by Professor Thomas Graedel from Yale University on the subject of **'Rare earths and other scarce metals: Technologically vital but usually thrown away'** The meeting will take place on Wednesday 20<sup>th</sup> March at Burlington House (further details are on pp 9, 10-11), and will also incorporate the ECG 2013 AGM.

Previous Chair's reports have commented on the changes in the RSC's interest group subscription model, where RSC members can now join up to three interest groups at no charge (beyond their RSC membership). This change has seen the **Environmental Chemistry Group's membership** grow to around **1600 members**, making it the largest subject interest group at the RSC. We have also seen some changes in composition and growth of the ECG committee, allowing us to run the wide range of events outlined above. The committee is always keen to hear from members, including feedback on events, suggestions for future activities, and other ideas, and we look forward to seeing you in 2013.

All members should **ensure that the RSC have their current email address/contact information** so they can be alerted when the ECG *Bulletin* is available *via* the ECG web pages, and receive notifications of other events. Under RSC rules, we (the ECG) are not allowed to hold these data. RSC member's details can be updated online on the RSC website or by contacting the membership department at [membership@rsc.org](mailto:membership@rsc.org).

**WILLIAM BLOSS**

December 2012

# The legacy of Rachel Carson

A report of the meeting to commemorate the 50<sup>th</sup> anniversary of *Silent Spring* held at the RSC's Chemistry Centre in London on 2 October 2012.

This joint meeting was organised by the RSC Toxicology Group and the RSC Environmental Chemistry Group together with The Institution for Environmental Sciences, and was supported by the RSC's Environment, Sustainability and Energy Division.

The aim of the meeting was to present a number of perspectives on how Rachel Carson's work contributed to the legislative, chemical and societal world we see today. Copies of the presentations from the speakers are available from the ECG website ([www.rsc.org/ecg](http://www.rsc.org/ecg)).

The meeting began with **Professor Andy Smith** (MRC, Leicester) giving a brief history of Rachel Carson's work. Amongst other details, he highlighted the difficulties of being a female scientist at that time. Carson first published on the environment in 1941 in her book *Under the Sea-wind* – recently republished by Penguin Classics, but it was not until her 1951 book *The Sea Around Us* (which won many prizes, and is also in print), that she attracted widespread public attention. She then became increasingly concerned with the effects of extensive pesticide use, culminating in the publication of *Silent Spring* in 1962. For the views expressed in this book, she was attacked by the chemical industry and even by the U.S. Department of Agriculture but was backed by President Kennedy's Scientific Advisory Committee in her findings. By this time, Carson was in poor health. She died in 1964, thus undoubtedly cutting short her contribution to the field.

One of the chemicals identified by Carson in *Silent Spring* was DDT. Professor Smith went on to give an overview of DDT use and toxicity. Prior to DDT, alternatives were either ineffective (e.g. pyrethrins) or highly toxic (e.g. arsenicals). DDT was first discovered in 1874 but it was not until 1939 that Paul Müller (Geigy, Basle) found that it was highly effective in killing insects. During the Second World War, DDT was a vital addition to the armoury in defeating malaria and typhus – diseases that could cause as many casualties as war itself. This fast-track use led to Müller being awarded the Nobel Prize in 1948. After the Second World War, the use of DDT escalated, and it was used as a widespread general-purpose insecticide in agriculture. The problems of DDT seemed to stem from overenthusiastic use with little concern for long-term consequences. With respect to human health effects, Carson was most concerned with cancer. DDT is slowly metabolised, with high doses causing tremors in



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humans, but it is a poor mutagen. To date there is weak evidence for DDT being associated with either liver or breast cancers, indicating that the threshold for any effects is far above current, and even historic, exposure levels. Most concern these days is with its potential reproductive effects as an oestrogen mimic.

Following Carson's work, DDT was banned in the US in 1972. Over the following decades, many countries across the globe followed suit, although some use continues today for indoor residual spraying to control malaria. However, even here there is ongoing controversy as to whether health effects are or are not being demonstrated. Professor Smith concluded that overuse and poor regulation of pesticides had profound effects on the distribution of chemicals in the environment and biosphere and that *Silent Spring* brought public and political attention to this and set in motion controlling and health regulations still with us today. However, pesticides (and other chemicals) are still required, and scientific risk assessment rather than risk perception should drive use and regulation of these substances.

In the next talk, **Dr Joe Rodricks** (Environ) gave a wider historical perspective with the title "In pursuit of safety: 100

years of toxicological risk assessment” (see pp 7-9 for Dr Rodricks’ article based on his presentation). Rodricks took us from Paracelsus, who identified that dose differentiates a poison from a non-poison, to Dr Alice Hamilton, who pioneered occupational epidemiology and industrial health in the early 20<sup>th</sup> century, and the 1906 Pure Food and Drug Act, which declared that food and drugs shall not contain adulterants that “may cause harm.” This Act led to the use of animal studies to characterise the effects of harm. Other pre-*Silent Spring* drivers of chemicals regulation included the recognition of occupational diseases (the American Conference of Industrial Hygienists, ACGIH, introduced exposure limits in the 1940s), the increase in post-war chemical production (leading to new safety requirements in the 1950s) and the identification of air and water pollution as a public health issue.

During the same period of time, cancers were also being studied and linked to chemical causes. By the 1950s there was a prevailing view that thresholds must exist for chemical toxicities, except for carcinogens, and Allowable Daily Intakes (ADIs) were being derived. These ADIs became targets even though no clear lines could be drawn between safe and unsafe and there is no way to quantify whether any reduction in exposures has led to adequate health protection. By the 1970s, a no threshold, linear dose model of cancer risk was adopted and, by and large, the system persists today. In 1983, the National Academy of Sciences issued the “Red Book” (Risk Assessment in the Federal Government: Managing the Process), which provided a standardised framework within which to undertake risk assessment. However, risk assessment *per se* does not enable decision-making. In 2008, the National Academy of Sciences published “Science and Decisions: Advancing Risk Assessment,” which calls for a unified and consistent approach to risk assessment. In the future, high throughput *in vitro* testing offers the potential for mode-of-action studies and better understanding of the inherent hazards of chemicals. In the continuing scientific and public debate about toxic hazards and their risks to health there is a need for greater, and improved, risk communication and public understanding of risk.

After lunch, the presentations moved from a historical perspective to the here-and-now. **Dave Bench** (HSE) started by giving an overview of UK pesticide regulations. Although pesticides have been used far back in history, their use did not become widespread until the 20<sup>th</sup> century. Before *Silent Spring*, pesticides were monitored through voluntary schemes such as the Crop Protection Products Approvals Scheme. These schemes developed over time but remained voluntary until the EC ruled that the UK was in breach of Community trading rules. This led to primary UK legislation, which has now been subsumed into the implementation of EU directives. The environmental risk assessment required for pesticide approval is rigorous, covering fate and

behaviour in soil, water and air as well as toxicity studies on a number of non-target wildlife species and micro-organisms. Pesticides have developed over the last 50 years – they are generally no longer broad-spectrum and more targeted on specific pest biology. The number of active ingredients has also been reduced through the re-approval process to around 300 active ingredients. Bench stressed that the process was not static but that there were continuing developments in EU legislation, independent scientific scrutiny and new scientific evidence.



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**Professor Alistair Boxall** (University of York) then discussed the uptake and transformation of environmental contaminants. Carson was concerned that residues persisted in soil for many years and that they could become widely distributed and transferred to humans through bioaccumulation in animals. Boxall explained that analytical developments were partly responsible for increasing concern around contamination; we are able to detect ever-lower amounts of chemicals in the environment. Looking at octanol:water partition coefficients to predict bioconcentration factors, it can be seen that many pesticides mentioned in *Silent Spring* would now be classed as persistent and/or bioaccumulative (DDT has a degradation half-life of about 17 years). In contrast, very few of the current “UK top 50” pesticides would fall into these descriptions.

Professor Boxall then turned to the transformation of chemicals. Pesticides degrade into other compounds that may be more or less toxic than the parent compound. Historically these transformation products have not been monitored. Many transformation products can, for example, be detected in surface water, and they are often more persistent than the parent compound. The octanol:water partition coefficients are quite reliable for assessing neutral compounds, but the uptake of other compounds is much more reliant on the pH of the surrounding environment and individual organism characteristics. This is potentially important as half of all REACH pre-registered compounds are not neutral. Boxall finished with a statement from Carson on the uncertainties

remaining and concluded that many of the points that she made remained valid.

Next, **Steve Edgar** (Vertase F.L.I. Ltd) presented a case study of contaminated land remediation at a former Bayer Crop Science site that was being redeveloped for housing. The site was heavily contaminated with agrochemicals, including pesticides and herbicides. During the public consultation, the work of Rachel Carson was raised and although there was an awareness of the issues there was little understanding. Nearby residents were concerned that remediation would churn up the contamination, rather than seeing the benefits of removing the contamination. A comprehensive site survey initially identified 217 chemicals of concern; this was prioritised down to 23. In total, about 1 million cubic metres of soil underwent processing, taking an average of 18 weeks treatment time. The risk communication issues with the public were the most challenging aspects of this work, and significant efforts went into communication and multi-agency co-ordination. The work was successfully completed with 96% contaminant removal from soil and more than 99% for water.

Following a refreshment break, **Professor Stuart Harrad** (University of Birmingham) looked at the changing profile of persistent organic chemicals. Whereas Carson was concerned with exposure to organochlorine pesticides, exposure profiles have since moved through polychlorinated biphenyls (PCBs) and dioxins and on to fluorinated and brominated compounds. Also, whereas historically environmental exposures have been mostly attributed to the diet, there is growing evidence that many of the new pollutants can be found in indoor dust as well, especially from flame retardants. For young children in the UK, exposure estimates indicate that intakes from dust would on average be similar to the dose from diet. However, 95<sup>th</sup> percentile dust exposures with a high dust intake would result in exposures three orders of magnitude greater than for diet. Studies correlating dust exposure and body burden are somewhat conflicting but both show a highly positive skewed distribution, with about 5–10% of samples/individuals more heavily contaminated. Some high-end exposure estimates for brominated diphenyl ethers (BDEs) show that guidance values might be exceeded, but the European Food Safety Authority (EFSA) recently concluded that current dietary exposure to hexabromocyclododecane in the EU does not raise a health concern and that additional exposure, particularly of young children, from house dust is also unlikely to raise a health concern. One of the challenges is the ongoing exposure due to extensive recycling and waste management of treated products. Furthermore, the chemical profiles are changing as new chemicals, such as chlorinated organophosphates, are introduced.

After a brief first-hand account of the still widespread use of DDT as a broad spectrum agricultural pesticide in Ethiopia, **Dr Keith Tyrell** (Pesticide Action Network UK) made a

case for how the current pesticide regulations had failed to restrict the use of neonicotinoid pesticides. He referred to a number of studies demonstrating an association between the use of neonicotinoids and collapses of bee populations and outlined the situation in Italy, where bee populations appear to have recovered following a ban on the use of neonicotinoids. Dr. Tyrell discussed the limitations of the current regulations, which are primarily designed to assess spray applications of pesticides, whereas neonicotinoids are usually applied as a seed treatment resulting in a systemic pesticide. Tyrell also stressed that despite uncertainties regarding the environmental safety of neonicotinoids, there were currently no plans to restrict their use. In Tyrell's view this was counter to the precautionary principle where the onus is on the manufacturer to demonstrate unequivocal safety, not for the public to demonstrate harm.

**Professor Ragnar Löfstedt** (King's College London) concluded the meeting with a précis of his recent paper on Risk versus Hazard in Europe. He outlined fundamental differences between Member States, and even regulatory bodies within Member States, as to whether chemical regulation should be hazard- or risk-based. Certain areas of Europe (for example, Scandinavia) were predisposed to taking a hazard-based approach to chemicals whereas others, such as the UK, were much more in favour of risk assessment. However, Löfstedt also described how a Member State's approach could differ depending on the circumstances. For example, the Swedish government has stated a desire to phase out all hazardous chemicals by 2020 (hazard-based) but has vigorously defended the eating of pickled herring, shown to be contaminated with persistent chemicals (risk-based). These positions are political; Sweden has a very small chemical industry so, as a nation, would not be overly affected by tighter chemical regulation whereas the consumption of pickled herring is an issue of cultural heritage. Löfstedt outlined the need for greater risk communication and highlighted a number of efforts to bring about a better understanding of risk across Europe.

The meeting provided a diverse exploration of the areas where Rachel Carson's work has had an impact. Several speakers showed that Carson was not instrumental in developing these ideas (much work had started before *Silent Spring*), but she did “shine a light” on the issues and generated a momentum for change that has had a huge impact on chemical development, regulation and environmental assessment. Her work has, for example, led to the use of less persistent and less bioaccumulative pesticides. However, uncertainties remain, for example in the assessment of chemical mixtures. Perhaps the greatest challenge is how to better communicate risk and improve public understanding of risk.

**KATE JONES** (Secretary of the Toxicology Group)

**JAMES LYMER** (Secretary of ECG)

# One-hundred years of toxicological risk assessment

A century of extraordinary progress in the worlds of pure and applied chemistry was, with the publication in 1962 of Rachel Carson's *Silent Spring*, suddenly called into question. Carson was by no means the first to raise alarms about the new kind of environment chemists had been creating since the introduction of structural theory in the late 1850s and the new science of chemical synthesis that quickly followed. But she was the first to do so in a way that resonated deeply with the public, and that powerfully activated their political representatives.

The decade of political activism following the publication of *Silent Spring* led, in the United States, to the enactment of major laws giving authority to newly established regulatory agencies to set legally enforceable limits on human exposures to chemicals in the workplace and contaminating the general environment.<sup>1,2</sup> These laws added to a host of laws that had been enacted in the pre-*Silent Spring*

era, requiring similar controls on pesticides (the principle but not the only subject of Carson's concerns), and regulation of chemicals used in foods, drugs, and consumer products.<sup>2</sup> The requirements set out in the new environmental and occupational health laws of the 1970s and 1980s, and increasing public pressure on food, drug, consumer product, and pesticide regulators, forced attention on a problem that public health and regulatory officials had been struggling with since passage of the first federal law mandating protection of people from unsafe exposures to the products of the new chemical industry: the Pure Food and Drug Act of 1906.<sup>2</sup>

The problem of identifying safe levels of human exposure to chemicals exhibiting toxicity (which virtually all chemicals will do at sufficiently high doses) could, after the 1970s, no longer be a matter of judgments by experts made out of public view, as it had been for the previous half-century. In the rest of this paper I will sketch out the history of our struggle with both the concept of safety, and with finding scientifically acceptable ways to apply the concept to ensure public health protection.

That chemicals could cause harm to health had, by the opening of the 20th century, been well established.<sup>3</sup> Since at least the 16th-century, following the famous insight of the Swiss pharmacologist, Paracelsus, that "all substances are poisons: only the dose separates a poison from a remedy", the importance of dose had been recognized. But until at least the 1950s little attention had been paid to the problem of identifying doses that were likely not to produce toxicity in a large and highly diverse human population. A number of efforts by public health officials during the first half of the 20th century led to the imposition of exposure limits on newly discovered contaminants in drinking water and foods, and recommendations for workplace exposure limits.<sup>4</sup> Significant air pollution problems emerged in the 1940s and 1950s in heavily industrialized urban areas, leading to widespread recognition of the need to control certain air emissions so that human health would not be put at risk. But none of these efforts and concerns was, until the 1950s, based on any explicitly described

methodology for establishing safe levels of exposure to chemicals.

By the 1950s, the problem was becoming significant, because the chemical and allied industries had begun to expand at a great pace and because air pollution related to the use of fossil fuels for energy production was beginning to skyrocket.

New laws relating to substances added to foods were passed in the 1950s, and these laws required that the Food and Drug Administration (FDA) decide whether substances added to food could be considered safe. Two leading FDA scientists, Arnold Lehman and O. Garth Fitzhugh, published a procedure that the agency would follow to make such a determination.<sup>5</sup> The two scientists recognized that toxicity information from animal studies (the use of animals for such purpose had begun to be studied in the early years of the 20th century) would often have to be the basis for establishing safe doses, because human data were either not available (as in the case of a newly introduced substance) or difficult to obtain. The FDA scientists offered two important insights. First, experimental animals could be expected to be less susceptible to a

*"For the first time in the history of the world, every human being is now subjected to contact with dangerous chemicals from the moment of conception to death."*

*Silent Spring, chapter 3*

chemical's toxic effects than would some members of a highly diverse human population. Second, variability in response to a toxic insult was likely to be large in the human population. Lehman and Fitzhugh introduced two "safety factors", each of magnitude 10, to account for these two important limitations in what could be learned from experimental toxicity studies. Thus came in the mid-1950s the Acceptable Daily Intake (ADI), established at 1/100 the maximum dose at which no adverse effect had been observed in animal testing.<sup>3</sup> The ADI would become the safe dose for humans. If a food additive was to be present in food at levels that, when the food was consumed, lead to human intakes less than the ADI established for that additive, the additive could be considered safe and approved for use.

Since then, much work has been done to refine the method used to derive ADIs, and the Environmental Protection Agency (EPA) has chosen to use the term Toxicity Reference Dose (RfD) instead of ADI. Nevertheless, the approach laid out by Lehman and Fitzhugh remained in place, and is still used widely to establish limits on human exposures to chemicals.<sup>6</sup>

The approach is, of course, based on the notion, implicit in the Paracelsus dictum, that certain "threshold" doses must be exceeded before a chemical's harmful properties can manifest themselves. The ADI and RfD are, in effect, assumed to be approximate threshold doses for large and highly diverse human populations. But, given the way they are derived, it is not at all clear that every member of the population is protected at exposures that do not exceed the ADI or RfD. Put another way, this approach provides no information regarding the fraction of the population that might be affected – might be at risk – at doses greater or less than the ADI or RfD. Thus, although the ADI/RfD approach is simple and has found much acceptance for decision-making, it is not truly a risk-based approach, that is, one based on an analysis of risk and a policy decision regarding the magnitude of risk that can be tolerated in different circumstances.<sup>7</sup>

Risk analysis and risk-based decision-making was not introduced into the area of chemical toxicity until the 1970s, and until recently had little effect on the safety assessment approaches we have been describing.

During the 1970s several authors began to emphasize the concept that safety is not an absolute.<sup>7</sup> If, for example, safety is defined as a condition of no risk, then it is, except in trivial circumstances, an empty concept, because such a condition can never be known. Those who espouse the use of the ADI or RfD for decision-making emphasize that it is not a sharp line between safe and unsafe exposures, but it is often used as if it were. New thinking on this matter has emerged and will be mentioned near the end of this paper.

The emergence of risk-based decision-making during the 1970s was in part prompted by the problem of carcinogenic

chemicals.<sup>1</sup> At least as early as the 1940s, many scientists and public-health officials had concluded that the behaviour of carcinogens was radically different from that of chemicals causing other forms of toxicity. The threshold concept was said not to apply to these especially dangerous agents, and "no safe level" was the official view of how they should be considered for decision-making purposes. Lehman and Fitzhugh asserted that ADIs should not be developed for carcinogens.<sup>5</sup> During the development of new food law's during the 1950s, the U.S. Congress included the Delaney Amendment, requiring a strict prohibition on the intentional addition to food of any substance shown to be a carcinogen.<sup>2</sup>

By the mid-1970s it had become clear that a relatively large number of chemical contaminants of the environment had carcinogenic properties and that some means had to be found to limit human exposures to them, because, unlike food additives or other intentionally introduced substances, there was no direct or simple way completely to eliminate human exposures. A number of proposals from the scientific literature led to the adoption in the mid-1970s, by both the EPA and FDA, of methods to estimate low-dose risks for carcinogens. These methods assumed the absence of identifiable threshold doses for carcinogens and a linear relationship between dose and risk<sup>3</sup>. Regulation would involve decisions regarding the magnitude of carcinogenic risk to be tolerated in different circumstances. A completely new, risk-based, approach to safety decisions was born. Safety was now seen, as it properly should, not as a matter of pure science, but as a policy choice involving decisions about risk toleration.

These ideas and their regulatory applications were controversial, and the U.S. Congress asked the U.S. National Academy of Sciences (NAS) to review the new risk-based approaches. A committee of the NAS issued, in 1983, a report (*Risk Assessment in the Federal Government: Managing the Process* – the "Red Book") that endorsed the new approach and that offered perspective and guidance on risk assessment and management.<sup>1</sup> The report became highly influential and set the stage for the following 30 years of chemical regulation. The power of the report's recommendations remains in effect today.

From the time of the issuance of the Red Book to the present, the science of risk assessment has taken on greater rigor, including the incorporation of methods based on knowledge of biological processes underlying the production of carcinogenicity or other forms of toxicity. Its use has expanded from chemical to other types of hazards, including microbial pathogens<sup>8</sup> and nutrients.<sup>9</sup> Greater clarity regarding the risk assessment/management distinction has also emerged.

Yet, controversy over both science and policy has accompanied these expanded and improved approaches, in part related to the complexities of the science underlying risk assessment, and in part related to the question of how risk

assessments should inform decision-making. Another study by the National Research Council, issued in 2009 under the title *Science and Decisions: Advancing Risk Assessment*,<sup>10</sup> has taken on these questions. The report is comprehensive with respect to both the science and applications of risk assessment and points the way to the future. It offers many recommendations and a new framework for decision-making that, if implemented, would do much to increase the utility of risk assessment.

The report also returns to the matter of safety assessments, as they have been traditionally undertaken. The authors show that a unified approach to risk assessment, based on a chemical's mode of toxic or carcinogenic action, can be applied. Quantifying risks for all toxicity endpoints is feasible, and, if implemented, can improve decisions. Within the new decision framework, the magnitude of risk reduction achieved with different approaches to managing risks can be understood for all forms of toxicity. With such understanding comes the ability to identify the most cost-effective approach to risk management. Such understanding cannot be achieved using RfDs as the guide. Furthermore, "safety" can be defined quantitatively, as the dose associated with a specified level of (presumably very small) risk. Whether and to what extent regulators move toward such a heavier reliance on quantitative assessments for public health decisions is unknown, but their decisions will be improved if they do.

To close where we began: perhaps Rachel Carson's most significant contribution to the whole enterprise of risk analysis relates to the fact that she was a superb communicator, and forced public attention on what is now universally acknowledged as a necessary component of risk-based decision-making. Decisions to protect public health can no longer be taken without full disclosure of their bases. All public health officials and manufacturers and users of chemicals have, thanks in great part to the influence of *Silent Spring*, the important responsibility of communicating to the public why their chemical risk management decisions ensure public health – and also environmental – protection.

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## JOSEPH V. RODRICKS

Environ, 4350 North Fairfax Drive, Suite 300,  
Arlington, VA 22203, USA  
jrodricks@environcorp.co

*This article is based on a presentation by Dr Rodricks at the RSC ECG & Toxicology Group meeting, The legacy of Rachel Carson, held at Burlington House on 2nd October 2012.*

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## 2013 ECG Distinguished Guest Lecture & Symposium – *The life cycles and criticality of scarce metals*. Thomas E. Graedel, Center for Industrial Ecology, Yale University, New Haven, CT

Chemists have studied and utilized the elements of the periodic table since Mendeleyev put them in the proper order in 1867. It is only recently, however, that the continued availability of some of them – rare earths, minor constituents of more common ores, those with significant toxicity, and so forth – has seemed problematic. Unlike the major metals (copper, zinc, etc.), relatively little information has been available concerning the technological utilization of these scarce metals: annual

rates of use, customary sources, principal commercial uses, rates of recycling, and the like. These contemporary properties of the scarce metals are being actively characterized in the Yale "criticality project". Recent results of this project, and the relevance of those results to the future supply and demand of the scarce metals, will be presented and discussed. (See pp 10-11 for the programme of the 2013 DGL and Symposium).

## Forthcoming Symposium

RSC Environmental Chemistry Group & RSC Environment, Sustainability & Energy Division

### 2013 Distinguished Guest Lecture & Symposium

#### Rare earths and other scarce metals: Technologically vital but usually thrown away

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A one-day symposium organised by the Environmental Chemistry Group and Environment, Sustainability and Energy Division of the Royal Society of Chemistry, incorporating the **2013 ECG Distinguished Guest Lecture**, to be given by **Professor Thomas Graedel** (Yale University)

Where: **The Royal Society of Chemistry, Burlington House, Piccadilly, London**

When: **Wednesday 20<sup>th</sup> March 2013**

**Programme:**

1200 Lunch and coffee

1300 Start of the meeting

**Professor Andrea Sella, University College London (UCL)**

*Terra Rara – The Elemental Unknown Sea*

**Mr David Merriman, Roskill**

*A Review of Global Supply of Rare Earths*

**Dr Mike Pitts, Technology Strategy Board [TSB]**

*Chemistry Innovation in Resource Efficiency*

1430 Tea/Coffee; **ECG Annual General Meeting**

1530 **Dr Adrian Chapman, Oakdene Hollins**

*Materials' Criticality – Mitigation Options and Impacts*

**ECG DGL: Professor Thomas Graedel, Yale University**

*Rare Earths and Other Scarce Metals: Technologically Vital but Usually Thrown Away*

**General Discussion (& Close at 1715)**

To register online, or to download a hard copy registration form, please see [www.rsc.org/ecg](http://www.rsc.org/ecg) and choose "Forthcoming Events". For further details please contact [s.t.wagland@cranfield.ac.uk](mailto:s.t.wagland@cranfield.ac.uk)

**Thomas Graedel** is Clifton R. Musser Professor of Industrial Ecology in the School of Forestry and Environmental Studies, Yale University. His research is centred on developing and enhancing industrial ecology – the organizing framework for the study of the interactions of the modern technological society with the environment. His textbook, *Industrial Ecology and Sustainable Engineering*, co-authored with B. R. Allenby, was the first book in the field and is now in its third edition. His current interests include studies of the flows of materials within the industrial ecosystem, and of evaluating the criticality of metals. He was elected to the U.S. National Academy of Engineering in 2002 for "outstanding contributions to the theory and practice of industrial ecology."

**RSC Environmental Chemistry Group****2013 ECG Distinguished Guest Lecture & Symposium – Rare earths and other scarce metals: Technologically vital but usually thrown away**

20<sup>th</sup> March 2013, Royal Society of Chemistry, Burlington House, London

Admission is by ticket only. In order to register for this meeting, please **register online** via [www.rsc.org/ecg](http://www.rsc.org/ecg) (choose “Forthcoming Events”) or complete the slip below and return by post (see details below).

There is a charge of £30 for members of the ECG and £60 for non-members of the ECG (£30 concessions, *i.e.* student/unwaged; proof required). Cheques should be returned with this form (made payable to *RSC Environmental Chemistry Group*). **Early application is encouraged as places are limited and will be allocated on a first come first served basis.**

A limited number of places are reserved free for retired members; these will also be allocated on a first come first served basis. **We are able to offer limited travel bursaries for current students – please email Dr William Bloss if you would like to be considered for one of these.**

Name .....

Affiliation .....

Address .....

.....

Email address .....

I would like to attend: ☐ Rare Earth Elements symposium

☐ The ECG AGM

I enclose a cheque for:

☐ £60 (non-member)

☐ £30 (ECG members/non-ECG concessions: RSC membership no: .....

☐ I would like to attend as a retired RSC and ECG member

Dietary/access requirements: .....

Signed ..... Date .....

**Please return to:** Dr Stuart Wagland, School of Applied Sciences, Building 40, Cranfield University, Bedfordshire MK43 0AL

Tel. 01234 750 111 Email [s.t.wagland@cranfield.ac.uk](mailto:s.t.wagland@cranfield.ac.uk)

## News of the RSC Environment, Sustainability and Energy Division

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In 2012, the Environment, Sustainability and Energy Division (ESED) has supported the work of its affiliated interest groups, including the Environmental Chemistry Group. For example, ESED sponsored the attendance of high profile speakers at the ECG Distinguished Guest Lecture & Symposium in March 2012, and an international speaker at the joint ECG–Toxicology Group meeting, which was held in September to celebrate the 50<sup>th</sup> anniversary of the publication of Rachel Carson's influential book, *Silent Spring*.

The RSC's work on solar fuels continued to receive support from ESED throughout 2012. A discussion meeting to mark the launch of an RSC report on Solar Fuels and Artificial Photosynthesis was held at Burlington House in May. ESED council member Professor James Durrant was one of around 70 participants who gathered to discuss important new solar fuels research and celebrate recent progress by scientists from across the world. Excerpts from the meeting were included as part of a BBC Radio 4 Frontiers programme on Artificial Photosynthesis, which is available to listen to online. The day culminated with a special lecture given by Professor Nathan S. Lewis, the George L. Argyros Professor of Chemistry at the California Institute of Technology and Editor-in-Chief of the RSC journal, *Energy and Environmental Science* on the technical, political, and economic challenges involved with widespread adoption of renewable energy technologies, which is also available online.

ESED held a successful joint Awards symposium with the RSC Analytical Division at the University of Hull in November, where Professor David Stuckey of Imperial College was presented with his medal for the Sustainable Water Award. Approximately 50 people attended to hear talks from

Professor Stuckey, Professor Aaron Wheeler (Joseph Black Award winner) and Dr Nicole Pamme from the University of Hull.

In 2013, ESED will support a meeting being run in Florida by the ACS Polymer Division on *Sustainable Polymers*. This meeting will bring together researchers in academia, industry and government laboratories together to discuss polymers and composites from renewable resources and green chemical processes. The meeting will take place from 20 to 23 May 2013. To register, please visit <http://polyacs.net/Workshops/13sustainable/home.htm> ESED will also be supporting the ECG Distinguished Guest Lecture & Symposium in 2013 on the topic of rare earth elements.

ECG members may be interested in a recent report published by the RSC on the topic of sustainable solutions to resource scarcity, called *Resources That Don't Cost the Earth*. The report is based on a 2011 workshop that brought together leading academics, industrialists, government agencies and policymakers from across Europe to identify challenges and solutions related to resource efficiency as well as opportunities for collaboration. [Available from <http://www.rsc.org/science-activities/resource-efficiency/resources-that-dont-cost-the-earth.asp>].

### Dr MINDY DULAI

Programme Manager, Environmental Science, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF

E-mail: [dulaim@rsc.org](mailto:dulaim@rsc.org)

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## Dr Trevor Pryce-Jones

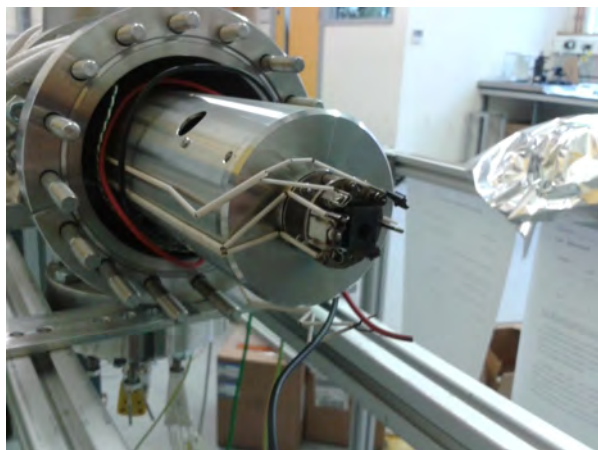
**Dr Trevor Pryce-Jones, CChem, FRSC**, retired Director of Studies, Chemistry Science, at the University of Hertfordshire, was treasurer of the RSC Environmental Chemistry Group from 1997 to 2000, and was a regular participant at our annual Distinguished Guest Lectures in London. We learnt with sadness of Trevor's death in September 2012.

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## Soft ionisation mass spectrometric techniques and the environmental sciences

A report of the meeting organized by the RSC Environmental Chemistry Group and the Molecular Physics Group from the Institute of Physics, held at the University of Birmingham on 7th November 2012.

The meeting attracted around 50 delegates, who managed to negotiate the tortuous location changes enforced by a major power failure at the University on the day – the only casualty ultimately being the tea and coffee. The meeting was motivated by recent advances in applying soft or chemical ionisation techniques, to permit improved sensitivity, identification and quantification of samples in (invariably complex) environmental matrices, and so offering substantial advantages over traditional approaches such as electron impact. Four invited speakers presented their work, including technical and methodological detail, followed by discussion and questions from the audience.

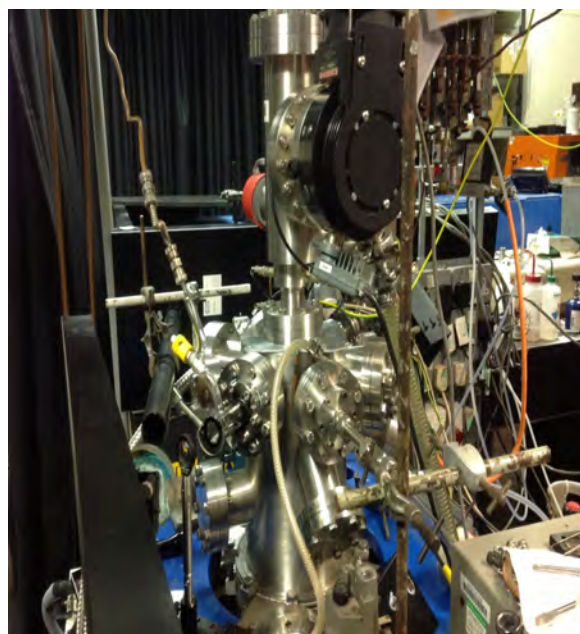


**A prototype Lithium Ion source at the University of Manchester. (Photo courtesy Carl Percival)**

**Professor Carl Percival** from the School of Earth & Atmospheric Sciences at the University of Manchester discussed *Development of Soft Ionisation Techniques for the Detection of Atmospheric Gases and Aerosol*. Carl gave an overview of his high-profile recent work using synchrotron radiation from the Berkeley National Laboratory Advanced Light Source as an ionisation tool to probe the reactions of Criegee intermediates – formed from alkene ozonolysis – with sulphur dioxide, which may enhance the production of sulphate aerosol in the atmosphere (Welz *et al.*, 2012). He then described the application of chemical ionisation mass spectrometry (CIMS), using  $\text{SF}_6^-$  and  $\text{I}^-$  reagents, for the detection of organic acids in the atmosphere, and concluded by

introducing a new potential “universal” chemical ionisation reagent, lithium ions, produced from a heated filament, which shows substantial promise for ambient and laboratory applications.

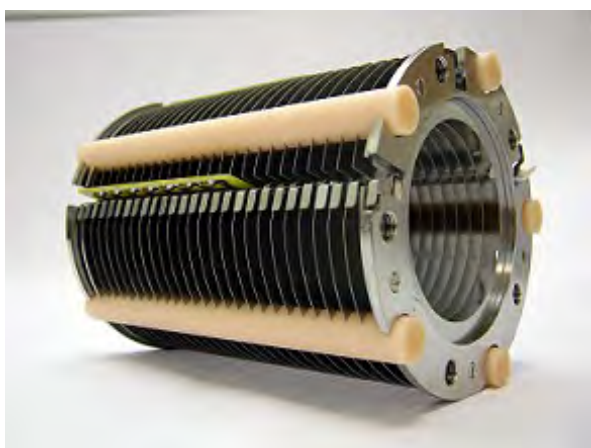
**Dr Mark Blitz** from the School of Chemistry at the University of Leeds then discussed *Unravelling kinetics and mechanisms of atmospheric reactions using soft ionisation TOF-MS*, and introduced his work using vacuum-ultraviolet (VUV) photoionisation coupled to time-of-flight mass spectrometry, where pulsed laser radiation at 118 nm has been used to study the laboratory kinetics of species ranging from  $\text{SO}$ ,  $\text{CH}_3$  and  $\text{CO}$  through to iodine oxides (e.g. Baeza-Romero *et al.*, 2010). Mark then discussed future detection possibilities which production of other photoionisation wavelengths – 157 and 126 nm from excimer-type laser systems, or OPO tunable radiation – could facilitate.



**The VUV-TOF-MS photoionisation mass spectrometer at Leeds. (Photo courtesy Mark Blitz)**

The third speaker was **Dr Fraser Reich** from Kore Technology Ltd, who under the title of *Improving the Sensitivity of a Soft Ionisation Technique* gave a fascinating account of the

reality behind the development (in collaboration with the University of Leicester) of a recent sensitivity enhancement to Proton Transfer Mass Spectrometry (PTR-MS), the RF Ion Funnel. This device reduces the loss of ions within the PTR reactor volume, prior to entering the mass selection region. Fraser's talk described the process from initial idea, through design & testing iterations, until finally the "light at the end of the funnel" (his words) was reached, with sensitivity increases of 1 – 2 orders of magnitude (Barber *et al.*, 2012).



**The prototype RF Ion Funnel developed by Kore. (Photo courtesy Fraser Reich)**

Finally, **Professor Paul Monks** from the Department of Chemistry at the University of Leicester, who spoke on *CIRMS from Urban Air Quality to Policy*, and gave a wide-ranging overview of the demonstrated scope and future potential for soft ionisation measurements, ranging from fingerprinting the composition of urban air, through character-

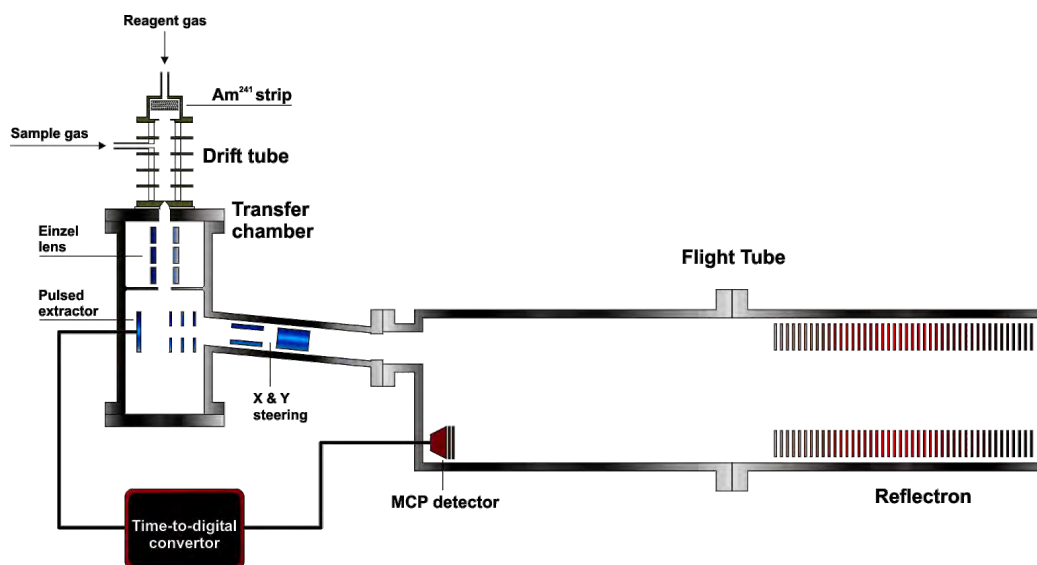
ising emissions from Mangoes during their ripening process (with apparently significant value for maximising the efficiency of supply lines) to forensic investigations and medical uses – the potential for exhaled breath analyses to provide non-invasive screening and/or diagnostic tests. Paul's presentation concluded with a review of the new scientific inputs and evidence which techniques such as soft ionisation mass spectrometry are making, and which then contribute to policy in bodies such as DEFRA.

**Users' Group:** As an outcome of the meeting, it has been suggested that a new "Soft Ionisation Mass Spectrometry Users Group" be (informally) established, for the exchange of experience and best practice on applications of PTR-MS and SIFT techniques in various research areas. Dr Emily House from Lancaster University will coordinate this, with support from the ECG & IOP Molecular Physics Groups, and members interested in receiving further information should pass on their details to Emily at [e.house1@lancaster.ac.uk](mailto:e.house1@lancaster.ac.uk)

**WILLIAM BLOSS**

## References

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- Oliver Welz, John D. Savee, David L. Osborn, Subith S. Vasu, Carl J. Percival, Dudley E. Shallcross and Craig A. Taatjes, 2012, *Science*, **335**, 204.
- Shane Barber, Robert S. Blake, Iain R. White, Paul S. Monks, Fraser Reich, Steve Mullock, and Andrew M. Ellis, 2012, *Anal. Chem.*, **84**, 5387.



**Schematic of a typical proton (or other chemical ionisation) time-of-flight mass spectrometer. (Schematic courtesy Paul Monks)**



## Forthcoming Symposium

# Recent Advances in the Analysis of Complex Environmental Matrices

Environmental Chemistry Group and Separation Science Group, Analytical Division

Thursday, 28th February 2013, Science Suite, Royal Society of Chemistry, Burlington House, Piccadilly, London

The meeting aims to cover the developments in analytical instrumentation that make it possible to simultaneously analyse numerous pollutants in complex environmental matrices with minimal sample clean-up.

### Programme

9.00 Registration and coffee

10.00 Professor Mark Viant (University of Birmingham, Birmingham, UK)

***Probing the water flea's biochemistry – a truly complex but high-information-content environmental sample***

10.30 Professor Ally Lewis (University of York, York, UK)

***Using comprehensive GC (GC x GC) in field devices for atmospheric chemistry***

11.00 Coffee

11.30 Dr Barbara Kasprzyk-Hordern (University of Bath, Bath, UK)

***Enantioselective analysis of chiral pharmacologically active compounds in urban water***

12.00 Dr Panayot Petrov (LGC Limited, Teddington, UK)

***GC-ICP-MS reference methodology to quantify polybrominated flame retardants in environmental waters relevant to the European Water Frame Directive***

12.30 Dr John Quick (Severn Trent Services, Coventry, UK)

***Analysis of non-polar organic compounds in water by GC-MS/MS***

1.00 Lunch break and sponsors exhibition

2.15 Professor John Dean (Northumbria University, Newcastle, UK)

***Analysis of VOCs in complex samples using thermal desorption-GC-MS/olfactory and GC-IMS***

Continued ...

2.45 Dr Chris Sparham (Unilever, Sharnbrook, Bedford, UK)

***Monitoring of cyclic volatile methylsiloxanes in the environment - an analytical challenge***

3.15 Nick Bukowski (ALMSCO International, Llantrisant, Wales)

***Characterisation of diesel exhaust particulates by high definition GCxGC-TOF-MS – classification and component speciation for toxicity assessment in humans***

3.45 Anthony Gravell (Environment Agency for England and Wales, Llanelli, Wales)

***Screening for pharmaceuticals and personal care products in effluents and surface water using LC-Q-TOF***

4.15 Meeting Close

***The meeting sponsor is Aligent Technologies UK***

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## **Recent Advances in the Analysis of Complex Environmental Matrices**

### **Registration**

Members of the Royal Society of Chemistry, Chromatographic Society or the British Mass Spectrometry Society: £60.00; non-members: £80.00; retired members: £30.00; students: £20.00

Registration includes all sessions, exhibition and lunch/coffee breaks.

Booking is on-line only : <http://www.rsc.org/ConferencesAndEvents/>

Booking page: <https://events.rsc.org/rsc/frontend/reg/tSelectBookingMode.csp?pageID=22859&eventID=97&tempPersonID=8380&eventID=97>

Event page: <http://www.rsc.org/ConferencesAndEvents/conference/alldetails.cfm?evid=112128>

Members of the two Societies are being given preferential rates with the following codes:

*Members of the Chromatographic Society:* 12IGMATRICESCS1

*Members of the British Mass Spectrometry Society:* 12IGMATRICESBMSS2

*Members of the RSC* – your RSC membership number

For further details or late registration if on-line booking has closed (you may only receive this Bulletin a few days before the meeting) please contact:

Dr Roger Reeve +44 (0) 191 515 2596 e-mail [roger.reeve@sunderland.ac.uk](mailto:roger.reeve@sunderland.ac.uk)

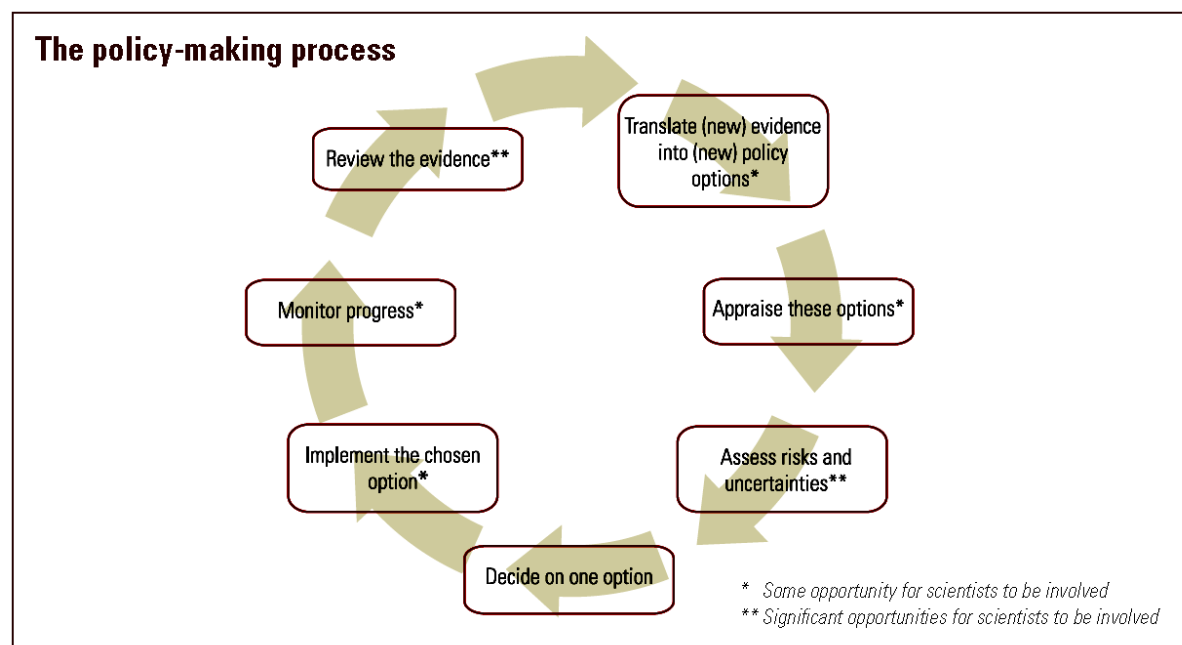
Professor Graham Mills +44 (0) 2392 84 2115 e-mail [graham.mills@port.ac.uk](mailto:graham.mills@port.ac.uk)

# Turning science into policy

This article is based on an invited lecture given by **Professor Paul Monks** to the RSC ECG Atmospheric and Environmental Chemistry Forum held in Leicester on 25<sup>th</sup> June 2012.

Science plays a crucial role in so-called “evidence-based policy-making”. The policy-making process (**Figure 1**) provides a number of opportunities for scientific engagement, from reviewing evidence to monitoring progress and assessing risk and uncertainty. Air quality is one area where environmental chemists are particularly active in informing the evidence-based policy making arena. Air pollution (**Figure**

forms to the government principles of scientific advice.<sup>3</sup> These principles are centred on understanding the clear roles and responsibilities of such committees: independence, transparency and openness. The applications of these principles are important in understanding the role of scientific advice in the complex areas of policy formulation and delivery. Scientific advisors have to respect the democratic man-



**Figure 1:** The policy-making process and opportunities for scientific input<sup>7</sup>

2) is a significant problem for the UK, with annual health costs of roughly £15 billion. Poor air quality reduces the life expectancy of everyone in the UK, as well as causing significant damage to ecosystems and historical buildings.<sup>1</sup>

In the Forum lecture, I overviewed the Air Quality Expert Group (AQEG) as an example of a scientific body contributing to the above process. AQEG is an expert committee to Defra (Department for Environment Food and Rural Affairs) that provides independent scientific advice on air quality, in particular the air pollutants contained in the air quality strategy for England, Scotland, Wales and Northern Ireland, and those covered by the EU directives on ambient air quality. AQEG gives advice on levels, sources and characteristics of air pollutants in the UK. It does not advise on health impacts or air quality standards that are within the remit of COMEAP.<sup>2</sup> As an integral part of its function, AQEG con-

date of the government to take decisions based on a wide range of factors and recognise that science is only part of the evidence-base that government must consider in developing policy. At the same time, government respects and values the academic freedom, professional status and expertise of its independent scientific advisors.

An example of the sort of advice these expert committees give, in the case of the Air Quality Expert Group, was the recent report on road transport biofuels and their impact on UK air quality.<sup>4</sup> Biofuels are superficially attractive as a means of offsetting greenhouse gas emissions through combustible materials that derive their carbon content from contemporary atmospheric carbon dioxide, but biofuels present wider issues with respect to sustainability. The EU has a biofuels directive that sets renewable targets for transport and the share of biofuels by the end of 2020. AQEG were

asked to comment on what are the likely biofuels and the combination of blends likely to be implemented. What is the evidence that biofuels change vehicle exhaust emissions and does this have an impact on air quality? How do exhaust emissions vary with blend strength and source material? What is the evidence from other countries for changes in atmospheric composition as a result of biofuel usage? Finally, what is the likely impact on air quality in the UK of the change in emissions as a result increased use of biofuels? After looking at the available scientific evidence, synthesising and providing expert opinion that weighs the risks and uncertainties of that evidence, AQEG concluded that the consumption of biofuels as low strength blends of up to 15% with “traditional” fossil fuels had little effect on air quality. It did point out that there should be markers of biofuels usage, for example, acetaldehyde, that could be monitored as part of routine air quality monitoring as an alert to change. It further noted there was substantial uncertainty about the effects of biofuels on vehicle emissions. If there was to be a move to higher strength blends of either bioethanol or biodiesel there would need to be a consideration of air quality impacts.

This short article demonstrates some of the processes and methodologies applied to develop evidence-based policy-making using air quality as an example. In the lecture, I gave further examples at the EU level as part of the air quality review process<sup>5</sup> and at the international level as part of efforts to understand the trade-offs between air quality and climate.<sup>6</sup> These examples demonstrate that scientific evidence and process is now a key aspect of policy development, formulation and delivery.

## References

1. See <http://www.defra.gov.uk/publications/2011/04/13/pb13378-air-pollution>
2. See [www.comeap.org.uk](http://www.comeap.org.uk)
3. See [www.bis.gov.uk/goscience-copsac](http://www.bis.gov.uk/goscience-copsac)
4. See <http://www.defra.gov.uk/publications/2011/04/06/pb13464-road-transport-biofuels/>
5. See [http://ec.europa.eu/environment/air/review\\_air\\_policy.htm](http://ec.europa.eu/environment/air/review_air_policy.htm)
6. See <http://www.igacproject.org/AirPolClim>
7. NERC, Science Into Policy, Jan 2011, see <http://www.nerc.ac.uk/publications/corporate/policy.asp>



**Figure 2:** Reducing harmful car emissions is a key aspect of air pollution reduction strategies. It is uncertain how use of biofuels will change vehicle exhaust emissions. Credit: Olegusk/Shutterstock

## Professor PAUL S. MONKS

Department of Chemistry, University of Leicester and  
Chair of the Defra Air Quality Expert Group (AQEG)

Email: [p.s.monks@le.ac.uk](mailto:p.s.monks@le.ac.uk)

# Bringing atmospheric chemistry to life for the new generation

A report of field work in Arctic Norway and classroom demonstrations

Teaching young people about atmospheric chemistry can be very rewarding, made easier by a continual presence of stories about climate change and pollution in the media and its inclusion in current GCSE syllabuses in chemistry, physics and environmental science. If today's children and young people can be taught to investigate, understand and care for our fragile environment this will lead to a new generation of responsible and passionate scientists. This article gives some examples of how the practical aspects of the topic can be approached with young people, from day exhibits in schools to an expedition to the Arctic. The equipment was funded by the £1000 Challenge, given by the RSC to its interest groups to devise their own activity to promote chemistry in the International Year of Chemistry. The work discussed here represents the contribution of the Environmental Chemistry Group to the Challenge.

Through one of British Exploring's expeditions (formerly known as BSES), I was able to lead a group of 10 young people carrying out an atmospheric science project. The expedition consisted of young people aged 16-20 and science and mountain leaders, totalling 75 people who spent either 3 or 5 weeks in the Finnmark region of Arctic Norway.

Our goal was to come up with "backpack" experiments requiring minimal equipment that could easily be carried over rough terrain to various camp sites away from the base camp of the expedition and even up onto the Oksfjordjokelen ice cap, up the steep glacial ascents, along with carrying camping equipment, radios, food rations and mountaineering kit. Another challenge was to compete in terms of excitement and goals with the mountaineering and survival challenges of living in this remote environment and to give our science a purpose and sense of reward and a feeling of investigating an area for the first time, like the field scientists of old who were in fact intrepid explorers.

**Right, Top-to-bottom:** Sampling river water; taking daily air sample; filtering glacier snow for particulate matter



This in fact worked out very well. The young people took to the science and had questions and their own explanations even when we were not in “science” mode. We took daily air samples for analysis for  $\text{CH}_4$  levels and  $^{13}\delta\text{CH}_4$  back in labs in the UK and diligently carried out a corresponding daily meteorological observation. We investigated pH, nitrate, nitrite, phosphate, sulphate, ammonia in rain water, snow and ice and in lakes and streams and found levels to be reassuringly low in this remote area. Ozone levels were also measured to be under 40 ppbv, and particulate matter deposition on the glaciers was investigated by filtering the snow. During a 24 hour science period with the other four groups on the expedition, we studied the hydrology of the region and the contribution of the glacial run off to the rivers.



**Top-to-bottom:** Testing soils and waters; descending off the glacier with plenty of air samples

Many of the young people in the “Atmospheric Group” were studying chemistry and physics at school or just starting at university, so it was important to connect these topics to daily life in the outdoors, even though these sciences, compared to geology and biology, are traditionally harder to explain visually in the environment. However, it was no surprise that the Atmospheric Group usually achieved the best radio communication with base camp by using their knowledge of radiowaves to position the aerials in the best locations. We also had the best handle on the weather and impending changes in wind direction and also kept a strict tab on any potential contamination of the local environment due to an understanding of the consequences of our activities on the water courses.

A science report was written after the expedition and the state of the environment compared to results from past literature. Also, air samples have been used to compare to air samples taken over the same period in Northern Scandinavia, including from aircraft science flights. The young people have come away with a feeling that science is a lifestyle and a way to get closer to our environment and, as the RSC says, “not all scientists wear white coats.”

Back at Leicester University we have pursued further projects with the same equipment, as well as other pollution monitoring equipment that would not have been sensitive enough to detect the levels of pollution in Norway. Several final-year undergraduate students have carried out atmospheric chemistry outreach demonstration projects at the National Space Centre, some local schools, a local museum and at the BBC Star-gazing Live demonstration activities at the University. Among these experiments are an aerosol simulation chamber (which demonstrates how a ‘smog’ cloud of secondary organic aerosol forms from the reaction of biogenic organics like limonene with ozone), a particulate matter filter (made from a coke bottle and a fish tank pump) and a tool for measuring the oxygen content of the atmosphere (quantifying the oxidation reaction of steel wool upon heating). Details of these demonstrations from the *Journal of Chemical Education* are included at the end of this article. These experiments proved to really engage children of primary and secondary school ages and enabled the students to discuss many aspects of atmospheric chemistry with the children.

These experiences show that with imagination and enthusiasm, it is possible to raise young people’s interest in atmospheric chemistry (and environmental science and chemistry in general). So go ahead, I encourage you to plan your own science experiments with British Exploring, or contact the Society to see if they could bring you back samples, or easier still, set up an outreach programme with local schools!

### Details of the equipment purchased for remote field work

1. Water quality testing kit: [http://www.lamotte.com/environmental\\_education\\_monitoring.html](http://www.lamotte.com/environmental_education_monitoring.html)

UK contact: [www.sword-scientific.co](http://www.sword-scientific.co)

2. Ozone monitoring badges: <http://www.ecobadge.com>

### British Exploring

[www.britishexploring.org](http://www.britishexploring.org) (applications for leaders, trainee leaders and young Explorers still open for summer 2013 and beyond to Himalayas, Oman, Norway and Iceland)

### Reference material for atmospheric chemistry experiments for demonstrations in schools

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### Acknowledgements

International Year of Chemistry £1000 challenge for the RSC Environmental Chemistry Group, and Rebecca Fisher at Royal Holloway University, London for  $^{13}\text{CH}_4$  analysis of the air samples.

Dr. ZOË FLEMING (zf5@le.ac.uk)

National Centre for Atmospheric Science (NCAS),

University of Leicester

Leicester LE1 7RH



**Demonstration equipment:** Limonene-ozone experiment to form aerosols

# Galligu: An environmental legacy of the Leblanc alkali industry, 1814-1920

## Introduction

The Leblanc alkali process was introduced into Britain in 1814 and it was to survive as a major industry until the early decades of the 20th century, by which time the technology had become obsolete. The importance of the Leblanc process was its use of salt to produce soda (sodium carbonate), replacing a reliance on natural sources such as barilla and kelp that were unable to meet the rapidly increasing demand for soda in the textile and soap industries.

The main soda production centres with Leblanc alkali works were Lancashire, Tyneside and Glasgow, all of which had easy access to the essential raw materials salt, coal and limestone. Almost from the start, and certainly by the early 1820s, as production of soda rose, people living close to the works began to accuse them of causing a “nuisance”. Initial

In the **Leblanc alkali process**, common salt was treated with sulfuric acid to make sodium sulfate and hydrogen chloride in two stages:



The sodium sulfate was heated with limestone and coal to produce “black ash”, which contained sodium carbonate, calcium sulfide, and some unreacted coal:



The sodium carbonate was extracted with water leaving *galligu* as the residue.

Initially released into the atmosphere, HCl from the Leblanc process was later utilised for the production of chlorine using the **Weldon process** and the **Deacon process**. By the early part of the 20<sup>th</sup> century, the Leblanc process had been replaced by the **Solvay process** as the manufacturing route for sodium carbonate.

## References

Kirk-Othmer *Encyclopedia of Chemical Technology*, 2<sup>nd</sup> edn., J. Wiley, New York, 1963, Vol. 1, p 710.

C. C. Gillispie, The discovery of the Leblanc process, *Isis*, 1957, **48**, 152

accusations concerned hydrogen chloride (or muriatic acid gas as it was called in the alkali trade), produced during the first stage and then dispersed from tall chimneys that became an important feature of these works. Releasing hydrogen chloride in this way without any amelioration proved a constant scourge for landowners and people living close by the works who were affected by the debilitating effects of the gas, as well as for manufacturers fighting the legal redress for the alleged damage inflicted. Failure on the part of manufacturers to control these gaseous emissions led in 1864 to establishment of the Alkali Inspectorate, the appointment of Robert Angus Smith as the first Inspector and a legal requirement to remove at least 95% of the acid gas from the gas stream released from chimneys.<sup>1</sup> However, another by-product, produced during the third stage, had not only just as deleterious an effect on the environment close to the works, but proved even more difficult to manage effectively. This was sulfur waste, or *galligu* as it was called by the people of Widnes, who were to suffer more than most from its unpleasant effects. In fact, effective treatment of *galligu* proved so elusive and the amounts of *galligu* produced were so great that remnants survive in the landscape to the present day.

Much has been written about pollution caused by acid gas (hydrogen chloride) and the associated court cases, but relatively little is known about *galligu* and the challenges it presented. This article considers the origin of *galligu*, its nature and chemical composition, its damage to the environment, the economic loss of sulfur in the waste, attempts to treat the waste, its removal in the 1970s and 1980s, and its environmental impact today.

## Origin and nature of *galligu*

*Galligu* was produced during the third stage, when the black ash (the product after heating salt cake, coal and limestone to high temperature in a revolver) was agitated with water (or lixiviated as it was known in the alkali trade). The sodium carbonate dissolved in the water, and the remaining residue was *galligu* – a wonderful onomatopoeic word to describe this black, evil-smelling, viscous material. In the alkali trade this waste was also referred to as sulfur waste, alkali waste, tank waste and vat waste, confirming its ubiquitous occurrence.



**Figure 1:** Sulfur waste heaps in 1985 at the Newton works of James Muspratt abandoned in 1851. Photo courtesy of Catalyst Science Discovery Centre.

Production of a ton of soda was accompanied by about 1.75 tons of *galligu* that contained about 15–20% of sulfur (originating from the sulfuric acid).<sup>2</sup> No attempt was made to recycle the sulfur in the waste, and while some *galligu* was dumped at sea, most was deposited on waste land adjoining the works, scarring the landscape and polluting the surrounding land, air and water (**Figure 1**).<sup>3</sup> As demand for soda for both consumption in Britain and for export rose dramatically during the nineteenth century so the quantities of *galligu* grew. By the 1870s the annual amount of this waste produced in Britain is estimated at close to 500,000 tons.

Over time *galligu* lost its sulfur content because of the chemical reactions with the atmosphere, ultimately yielding a white and rather friable material unable to support any significant load.

### Damage to the environment

When freshly deposited, the sulfur waste was mainly calcium sulfide. This was unstable in the atmosphere and by a series of chemical reactions, which were dependent on the composition of the atmosphere, formed a friable mixture of undecomposed sulfide, calcium sulfate, calcium chloride, calcium carbonate and calcium hydroxide.<sup>4</sup> In wet weather, any acid gases such as carbon dioxide (carbonic acid) or, as frequently happened, hydrogen chloride from the alkali works reacted in the rain with the sulfur waste to release copious quantities of hydrogen sulfide, a highly toxic gas recognized by its characteristic smell of bad eggs. The reaction with acidic rain is exothermic, but even in very dry weather the waste was found to heat up and could eventually catch fire, releasing large quantities of the pungent gas sulfur dioxide. The Alkali Inspector reported some fires burning almost continually for several years.

The environmental consequences of *galligu* in Widnes are vividly described by Robert Angus Smith in his report to the 1876 Royal Commission on Noxious Vapours:

The town of Widnes is very frequently, if not at all times, subjected to the influence of sulfuretted hydrogen [hydrogen sulfide] ... The tank waste, composed of sulfur and lime in various states of oxidation, is used for raising up the low lands on the Mersey and forming a foundation for future buildings. The drainage of lands thus treated is offensive: it has a yellow colour, and on exposure to air gives out the gas complained of. At certain spots the streams meet with acid streams, and the gas is then given out in enormous quantities. I have observed one spot, but I believe there must be others underground, perhaps also over-ground.<sup>5</sup>

The copious quantities of sulfur dioxide and hydrogen sulfide added to the black smoke from burning coal to produce a cocktail of pollutants that gave Widnes (and some other towns) its characteristic unpleasant smell and pall of black smoke. It may be because of the presence of these gases that Robert Angus Smith reported:

It is true that those coming to Widnes even from very dark and gloomy skies enter that town with a certain awe and horror ... and wonder if life can be sustained there.<sup>6</sup>

### Economic loss of sulfur

*Galligu* contained up to 90% of the sulfur from the sulfuric acid in the first stage, yet until the later 1830s no attempts were made to regenerate any of the sulfur and recycle it to produce more sulfuric acid. Sulfur was not only an important raw material but also very expensive. It was mainly imported from Sicily and the price could fluctuate wildly; in 1832 the price rose by 163%.<sup>7</sup> To safeguard regular supplies at stable prices, several manufacturers, including James Muspratt (Liverpool and Newton works) and Charles Tennant (St. Rollox works in Glasgow), purchased sulfur mines in Sicily, but in retaliation the King of Naples sequestered all the sulfur mines to preserve his monopoly. This intervention provoked action by the British Foreign Secretary, and part of the British fleet was dispatched in an attempt to enforce extant trading agreements between Britain and Naples, but to no avail. The uncertainty of supplies from Sicily prompted British manufacturers to turn to iron pyrites (and later copper pyrites) as a source of sulfur, and this spawned a separate industrial sector within the Leblanc alkali industry concerned with processing metals that included copper, silver and gold.<sup>8</sup> Later in the nineteenth century when the alkali and

bleaching powder products became uneconomic, the Leblanc industry survived through the sale of these metal products.

### Attempts at treatment

Most Leblanc manufacturers were not trained chemists, and they used the process as a simple recipe, following the different stages with the set quantities of raw materials and appropriate operating conditions to produce soda and disregarding other products that were deemed waste. Even with the important economic value of sulfur for sulfuric acid, it is very unlikely that any consideration was given to recycling the sulfur from *galligu*. Developing suitable recycling processes was left to a few inventive geniuses.

In 1837 William Gossage, who had invented the acid tower for condensing hydrogen chloride in 1836, patented a process for treating sulfur waste after suffering the problems of disposal and costs at his alkali works in Worcestershire.<sup>9</sup> Gossage's approach was to treat the waste with carbonic acid (an aqueous solution of carbon dioxide) to produce hydrogen sulfide. This was then burnt to form sulfur dioxide, which was fed back into the lead chamber for the production of further quantities of sulfuric acid. His patent included the enlightened proposal to store the hydrogen sulfide in a gas-holder until it was needed as a way of controlling the reuse of the gas.

The process worked well on the small scale, but proved much more difficult to operate effectively when scaled up, given the sheer quantity of waste to be processed. There were two main drawbacks: the technical inability at the time to pump large quantities of gases, and the gradual dilution of the hydrogen sulfide in the gas stream due to the large quantities of carbon dioxide. James Muspratt was persuaded by Gossage to start using this process but it proved an expensive error of judgement:

You are aware that Mr. Gossage stated to me that £500 worth of apparatus would recover the sulphur from our waste, and about £5000 now has been expended, and the tenth part of sulphur is not yet recovered, though we are nearly at full work.<sup>10</sup>

For Gossage the cost was much greater. Having persevered for some time he was reputed to have spent £22,000 over many years trying the perfect the process.<sup>10</sup>

The next major process was developed by Ludwig Mond and patented in 1861. Mond was born in Cassel, Germany and studied with Hermann Kolbe in Marburg and with Robert Bunsen in Heidelberg. Like Gossage, Mond had an inventive and tenacious mind when it came to finding working solutions to technical problems. Mond's process involved blow-

ing air through the sulfur waste to convert the calcium sulfide into "calcium sulphhydrate" [probably a mixture of polysulfides and sulfur oxyanions, which included 'calcium thiosulfate'; see *J. Chem. Soc.*, 1873, **26**, 197-200] and then precipitate the sulfur by treatment with excess hydrochloric acid (available in large quantities from "acid towers" at the alkali works).<sup>11</sup> Mond claimed the process could recover 50-60% of the sulfur, but in practice it was closer to 40%.<sup>11</sup> The process was taken up by several manufacturers, but Mond had hoped to persuade Robert Angus Smith and the Alkali Inspectorate that the process should 'be adopted by law to prevent the loss of sulphur ... just as the 1863 Act had tackled the release of hydrogen chloride gas with the adoption of Gossage (or "acid tower")'.<sup>12</sup> Unfortunately the process proved too expensive and not sufficiently reliable to be included in the regulations of the Alkali Inspectorate, although in 1869 the Rivers Pollution Commission did endorse Mond's process.<sup>12</sup>

Another approach to regenerating the sulfur from waste was developed in 1871 by James McTear, manager at Tennant's St. Rollox works, near Glasgow. It involved pumping the liquors from the waste heaps into special vessels, treating them with sulfurous acid and then precipitating the sulfur with hydrochloric acid. It proved reliable in operation and cheap to install; it was adopted by many manufacturers even though it only recovered between 27 and 30% of sulfur. Without more effective treatment processes, *galligu* continued to be dumped in ever-increasing quantities, adding to the unhealthy atmosphere surrounding the alkali works. The Annual Report of the Alkali Inspector for 1885 highlighted that:

There were nearly four and a half million tons of alkali waste in Lancashire alone and that it was increasing at the rate of 1,000 tons a day.<sup>13</sup>

A really effective process to handle the large quantities of waste did not emerge until 1888, when the Claus-Chance process was developed, based in part on Gossage's process of 1837. On 29 June 1882, C. F. Claus registered a patent for 'obtaining sulfur from sulphide of hydrogen' (BP 3608/1882), following his work on the removal of hydrogen sulfide from coal gas. But Alexander Chance (alkali manufacturer at Oldbury) had seen this patent listed in the *Journal of the Society of Chemical Industry* of 29 April 1883 and felt it might be relevant to the recovery of sulfur from alkali waste. Claus's patents were controlled by Ammonia Gas Purifying and Alkali Company Limited, and on 10 July 1883, Chance finalized terms for a licence. Two days later, while attending the Annual Meeting of the Society of Chemical Industry in London, several members visited the works of the South Metropolitan Gas Company to inspect the experimental set-up of the Claus kiln.

Even though the principles of the process were straightforward, getting it to operate efficiently on a continuous basis with the large quantities of alkali waste proved elusive. Chance confessed that ‘though the problem seemed simple on paper, four years of labour and the further expenditure of several thousands of pounds were necessary before he was able to make pure sulphur from alkali waste on a manufacturing scale and at an economical cost’.<sup>14</sup> Claus registered another four patents in perfecting the process. As Alexander Chance described the overall operation:

The process is performed by mixing sulfuretted hydrogen with a *regulated quantity* of air, and sending the mixture of sulfuretted hydrogen and air through a layer of anhydrous oxide of iron, which, by the heat generated by the reaction itself is maintained at a dull red heat, the oxide of iron itself undergoing no change. Free sulfur being obtained in the fused or sublimed form, according to the temperature of the kiln and of the depositing chamber.<sup>15</sup>

It was found that 60-80% of the sulfur could be recovered from the waste, a much more effective process than any of its predecessors, and it proved more reliable.

### Removal and amelioration

Sulfur waste has remained very resilient in the environment from its 19th century production. Its presence survives to the present day even though it is now in a chemically stable state. While its use in farming failed and some was dumped at sea, *galligu* found application in a number of places for levelling ground (see **Figure 2**). The main phase of removal came with the major land reclamation schemes of the late 1970s and early 1980s, which made a concerted effort to remove the blight of derelict industrial sites. Although the Muspratt works on the banks of the St Helens Canal at Newton was dismantled in 1851, the mounds of sulfur waste were still present in the early 1980s and were only cleared as a result of a land improvement scheme for the St. Helens Canal.

As part of the amelioration of industrial sites, the Botany Department at the University of Liverpool under Professor Tony Bradshaw conducted many studies to discover whether it was possible for plants to grow on different waste tips and derelict land left from industrialization. As we have seen, areas used to dump *galligu* became very calcareous and the pH changed over time from below 7 to above 7. One study on a *galligu* waste area in Bolton showed a rich diversity of plant species, including some quite rare orchids.<sup>16</sup>



**Figure 2:** The extensive area of sulfur waste in Ditton (Widnes) designated the Ditton Alps by the Planning Department of Halton Borough Council. Image courtesy of Halton Borough Council.

### Impact today

The initiatives of the 1970s and 1980s removed the major heaps of *galligu* but not the vast majority of the *galligu* used to level ground or dumped near former sites of alkali works, and so *galligu* can be found today in Widnes, a major centre for the Leblanc industry during the nineteenth century. It is not readily evident to the naked eye but lies just beneath the surface of golf courses, parkland and other open ground. Its hidden presence is evident from the undulating road surfaces and the warning road signs on the A562 main road between Liverpool and Widnes. The *galligu* will remain for some time as a legacy of a once important industry that has long disappeared.

### References

1. Alkali Works Act 1863 and appointment of Robert Angus Smith in 1864.
2. C. T. Kingzett, *The History, Products and Processes of the Alkali Trade*, Longmans, Green and Co., London, 1877, pp. 133-134.
3. Letter to James Muspratt from John Clow, dated 4 August 1836. (Ref: 920/MUS/2-37, Muspratt Papers, Liverpool Record Office.). Some sulfur waste from Tyneside works was dumped at sea.
4. The chemical composition of sulfur waste was complex. Besides containing unreacted coal, the waste contained about 40% of calcium sulfide when first deposited. Over time and under the action of carbon dioxide in the air (or carbonic acid in rainwater), the waste became calcium carbonate. By the 1980s, the surviving mounds had a very friable consistency.

5. Robert Angus Smith, Intermediate Report of the Chief Inspector, 1863 and 1874, of his proceedings since the passage of the latter Act. Parliamentary Paper 1876 (165), p. 3.
6. 12th and 13th Annual Reports of the Alkali Inspector to Parliament. Parliamentary Paper 1878-79 (C.2199), pp. 10.
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8. The introduction of iron pyrites required a redesign of the hearth used for burning sulfur.
9. On 17 August 1837, William Gossage filed British Patent 7416/37 for the treating sulfur waste and regenerating the sulfur as sulfur dioxide.
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11. L. F. Haber, *The Chemical Industry during the Nineteenth Century*, Clarendon Press, Oxford, 1958, p. 99.
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16. E. F. Greenwood (ed.), *Ecology and Landscape Development: The Mersey Basin*, Liverpool University Press and National Museums and Galleries on Merseyside, Liverpool, 1999, p. 74.

**PETER REED**

Leominster, Herefordshire

Email: [peter@peterreed.plus.com](mailto:peter@peterreed.plus.com)

*This article is based on a presentation by Peter Reed at the Royal Society of Chemistry Historical Group Meeting: "Where there's muck there's brass", which was held at the Chemistry Centre, Burlington House, London, on March 23<sup>rd</sup>, 2012.*

**RSC** | Advancing the  
Chemical Sciences**Environmental Science: Processes & Impacts**

The RSC journal *Journal of Environmental Monitoring* was retitled from the beginning of 2013 (volume 15). The new name for this journal is *Environmental Science: Processes & Impacts* (*Environ. Sci.: Processes Impacts*).

The change of name is intended to emphasise the broad scope of the content of the journal on environmental matters:

**1. Source, Transport and Fate**

For example: emerging contaminants; source characterisation; biotransformation; chemical/physical transformation; presence and activity of metabolites; soil and aquatic science; metal speciation; atmospheric science; and climate change.

**2. Exposure and Impacts**

Given that the environment has natural, rural and urban components including homes and workplaces, what is the toxicological significance of emerging contaminants and other compounds in the environment?

**3. Policy and Legislation****4. Novel Analytical Tools and Measurement Technologies****5. Sustainable Solutions and Technologies (Resource management)**

The first issue in 2013 of *Environmental Science: Processes & Impacts* was dedicated to the theme of 'Anthropogenic nanoparticles in the environment'.

# Organic waste recycling – an opportunity (and a challenge) for the chemical industry

## Introduction

The legislative and fiscal dynamics of the waste management sector in the EU have resulted in a major realignment from disposal in landfill sites to recycling and recovery. The main objective of these changes is to minimise the impact of waste production on climate change. Under the revised Waste Framework Directive (rWFD), Local Authorities in the UK are obliged to adopt waste policies that divert waste from landfills. This shift in waste management policy means that waste is increasingly seen as a resource with which to produce secondary end products. Organic waste recycling, in particular, offers the UK an opportunity for launching new technologies and industries.

The Waste Resources Action Programme (WRAP) estimates that 25% of the 100 million tonnes (mt) of waste arising in the UK is organic in nature. Over the past five years, the UK has seen a growing momentum within the anaerobic digestion (AD) industry, which processes various feedstocks, such as on-farm crops and industrial and non-industrial organic waste and sewage.<sup>1</sup> In the UK in 2011, 3.7 mt of non-hazardous waste from both municipal and commercial sources was fed into 46 AD plants, producing 54MW electricity.

Of the remaining 21 mt, ~8.5 mt were processed in the organic recycling industry, providing compost and soil improver for agriculture and landfill caps,<sup>2</sup> and 4.6 mt were recovered as waste wood. The residual 8 mt remained commingled with the balance of the waste stream, and were largely sent to landfill.

As an example of the scale of the opportunity within the UK, it is estimated that over 300 kilo tonnes of renewable chemicals, such as 1-butanol, acetone and hydrogen, could be produced from the organic waste currently sent to domestic landfills.

## The challenge for organic waste recycling

Nongovernmental Organisations are pushing for a zero bio-mass to landfill policy. To achieve this, the waste management infrastructure must quickly develop to remove the bio-mass currently sent to landfill from the balance of the waste stream. Only a small fraction of this volume is likely to be

segregated at source due to the increased cost and complexity that source segregation presents in the waste management supply chain. The majority can be recovered in facilities such as mechanical biological treatment (MBT) Plants.

Organic waste is inherently variable in composition, depending upon geography, time of year and the myriad of treatment processes employed. This presents legislators with a difficult challenge and innovators with an opportunity. Typically organic waste has a moisture content >50% (e.g. a typical vegetable is >80% water). The balance of material in the organic waste is a combination of fermentable organic matter (primarily cellulose and hemicellulose), proteins, fats and non-fermentable matter (lignin, ash). The high moisture content of organic waste makes it unsuitable for thermal treatment processes such as Energy from Waste (EfW).

## Fermentation technologies for organic waste recycling

Fermentation of the wet organic fraction of waste biomass is an economically viable route for producing chemicals from waste – particularly in the UK, where alternative feedstocks are either not available in sufficient quantity (grains and sugars) or the cost is prohibitive (grain straws and stover). An example of a successful technology in the UK for the reuse of organic waste is the production of 1-butanol.

In 1916, Chaim Weismann [1874-1952; later the first President of Israel, 1949-1952] isolated an anaerobic microbe, *Clostridium acetobutylicum*, ATCC 824, which can convert sugar and simple starches into, *inter alia*, acetone, 1-butanol, ethanol, hydrogen and carbon dioxide. This process, known as the ABE [acetone-butanol-ethanol] process, was commercialised during the First World War, because it was the only known route for the production of high volumes of pure acetone needed for cordite manufacture for use in munitions. With the emergence of the petrochemical industry, the ABE process suffered a relative decline for production of bulk chemicals. However, the opportunity offered by organic waste recycling has led to chemical companies such as Solvext adopting the ABE fermentation process for the pro-

duction of chemical intermediates, including 1-butanol, from organic biomass.

Solvert has pioneered a continuous feedstock pre-treatment technique in the ABE process, which overcomes a number of the problems associated with traditional batch hydrolysis systems. The aim is to produce a feedstock stream containing fermentable matter with the minimum amount of enzyme inhibitors and non-fermentable matter entrained. This stream is required to meet the end of waste regulations,<sup>3</sup> enabling it to be used freely as a feedstock for a number of downstream processes from chemical syntheses to simple anaerobic digestions.

### The chemical market

By adapting a tried and tested industrial biotechnology process, Solvert has created a commercially viable supply chain and process technology. These processes can also be implemented in developed countries, and provide existing markets with new products while resolving the issues around waste management.

Solvert chose 1-butanol as the primary target product because it has an established chemical market (\$4.5 billion per annum) that, in certain applications, is demanding a renewable alternative to the petrochemical-derived product. 1-Butanol is currently manufactured by a number of the world's leading chemical companies (Dow, BASF and Eastman) by gasifying propylene and using the resultant syngas in the OXO alcohol process. In the first half of the 20th century, 1-butanol was manufactured using a fermentation process. A number of companies, for example HC Sucroquímica (HCS) in Brazil, have re-commercialised the ABE process leveraging their feedstock knowledge and facility integration (Figure 1).

HCS is a family-run sugar refinery in Brazil that has an integrated sugar production plant and ethanol distillery, and in 2006-2007 constructed a modern ABE facility using sugar cane juice as feedstock. The plant operates on a seasonal

basis, supplying renewable 1-butanol and acetone for Brazil's domestic chemical market.



**Figure 1:** HC Sucroquímica's ABE fermenters (reproduced by permission of HC Sucroquímica)

Production today is focused on sugar cane juice, but HCS is already developing their second generation process to use the surplus bagasse from their sugar refinery.

Once the "Waste to" concept has been established with 1-butanol, Solvert has identified a number of other chemicals that can be manufactured by fermentative processes using molasses derived from waste as a feedstock – for example lactic acid, ethanol, isobutanol and succinic acid.

### The advantages of organic waste recycling

Diverting wet waste biomass from landfill and other low/no value applications into the chemical supply chain offers waste stakeholders significant advantages over conventional waste management technologies:

1. Avoids organic waste going to landfill sites.
2. Reduces the costs associated with waste management collections:
  - a. Reduces the number of bins required, enabling combined collection of mixed food and garden waste without compromising animal by-product regulations;
  - b. Applies to multi- and single-occupancy dwellings alike, helping to make resource management available to all members of the community;
  - c. Reduces the requirement for enforcement of source segregation, as the process is tolerant of non-targeted contamination in the collected stream;



- d. Provides cost surety and control, allowing more accurate forecasting and budgeting within local authorities.
3. Creates a new higher value market and use for co-mingled organic waste diverted from landfill.
4. Allows effective removal of the wet fraction from the residual waste stream, leaving a dryer material and maximising net calorific value and materials recovery.
5. Removes the odour and health risks from bio-aerosols associated with aerobic composting systems.
6. Adds value to the resource management system, giving opportunity for economic regeneration and creation of real long-term, productive manufacturing jobs.
7. Incorporates a sustainable water management system.
8. Deploys proven, open-ended technology, future-proofing investment in waste management as technology develops.

Establishment of waste-to-chemicals facility diverts ~150,000 tonnes/year of biomass from landfill, resulting in ~210,000 tonnes/year CO<sub>2eq</sub> greenhouse gas emission savings when combined with the petrochemicals removed from the chemical supply chain.

Because Solvert's process targets a feedstock that is geographically dispersed, the technology has been conceived to support small regional production facilities rather than large central facilities. Each local facility will create 25 skilled jobs and support a much larger number of auxiliary jobs in the local community. Minimizing the transporting of waste provides a number of benefits including satisfying the proximity principle of waste management, lower carbon emissions due to logistics and lower logistics costs.

Diversion of biomass from landfill will prolong the life of the existing permitted landfills within the UK, enabling them to receive the material not suitable for recycling or energy recovery. By including extensive water treatment in each facility, Solvert would also remove the risk of leachate and groundwater contamination from landfill, because the wet fraction of waste would be diverted to a facility where the water component was treated and eventually returned to the water course at an appropriate standard.

Finally, establishing a sustainable supply of base chemical building blocks to the UK chemical manufacturing industry will support the creation of a niche renewable chemical mar-

ket within the wider petrochemical market, underpinning growth and investment in the UK chemical industry.

## Solvert

Solvert was founded in July 2010 to develop technology that could exploit the waste management supply chain in developed countries. Our technology also works in low-cost environments. However, as Solvert's founder is a chemical engineer, the company has long-term objectives to build, own and operate manufacturing facilities in the UK to support the UK's bioeconomy.

Solvert is based in the Wilton Centre, Redcar, formerly ICI's Research and Development Headquarters. The Wilton Centre is the home of the Centre for Process Innovation and the National Industrial Biotechnology Facility (NIBF), which were developed by the UK government to provide facilities and support small and medium enterprises in industrial biotechnology. Solvert's business plan has been built around using NIBF to demonstrate our technology at a commercial scale.

Solvert is currently raising finance for the next stage of its business development, which takes the technology already demonstrated at lab scale and moves it into the NIBF for scale-up and demonstration.

## References

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**KRIS WADROP** (kris.wadrop@solvertltd.co.uk)

*This article is based on a presentation by Kris Wadrop at the Environmental Chemistry Group 2012 Distinguished Guest Lecture and Symposium held in the Science Room at Burlington House on Wednesday, March 14<sup>th</sup> 2012.*

## Meeting report

# ECG Atmospheric and Environmental Chemistry Forum

The Environmental Chemistry Group held its third Forum for early career researchers in atmospheric and environmental chemistry at the Department of Chemistry, Leicester University on Monday, June 25<sup>th</sup>, 2012. The event was attended by PhD students from numerous British universities. All delegates gave either a 15 minute talk or a poster presentation on their own research. Delegates had ample time to network and exchange expertise and opinions during lunch, the poster session and the careers discussion.

The Forum's invited keynote lecture **Air quality: turning science into policy** was given by Professor Paul Monks (Leicester University), who provided an informative insight into the mechanisms through which scientific understanding informs legislation and policy. This subject was particularly appropriate for an ECG Forum because "policy" is a vitally important end-use of research knowledge, yet one that is typically beyond the experience of researchers at the early stages of their careers.

After the keynote lecture, there was a wide-ranging careers discussion facilitated by an "expert panel" comprising Prof. Mat Evans (York University), Dr Helen Walker (AEA Technology) and Charlotte Ashley-Roberts (RSC careers adviser). We are grateful to our experts for contributing their time, experience and enthusiasm. We acknowledge an award from the RSC Travel Grant Scheme that enabled the organisers to offer student bursaries to attend the Forum, and sponsorship of some of the Forum's costs by NERC's National Centre for Atmospheric Research.

Below we present a selection of abstracts from the Forum delegates' talks and posters. The abstracts were provided by the forum delegates and compiled and edited by Stephen Ball and Bill Bloss. Additionally Prof. Monks has written a short summary article based on his keynote lecture; his article appears on page 17 of this edition of the ECG *Bulletin*.

## Section 1: Field studies and ambient air measurements

### 1. Investigating Air Pollution in London

Rachel Holmes, Richard Lidster, Jacqueline F. Hamilton, James D. Lee and James R. Hopkins  
Department of Chemistry, University of York

The majority of the World's population lives in polluted urbanized areas. Poor air quality is shortening the life expect-

tancy of people in the UK by an average of 7-8 months and costs the UK economy around £20 billion per year.<sup>1</sup> Despite this, our understanding of the atmospheric processing of pollutants in urban environments and their effect on air quality remains poor. The Clean Air for London (ClearfLo) project aims to investigate boundary layer pollution across London and thus improve the prediction capability of air quality models. Numerous previous studies in urban environments show discrepancies between the observed concentrations of short-lived atmospheric radicals and values calculated using explicit chemical models. One possibility is that copious reactive sinks for radicals are missing from the models, and one candidate is unmeasured volatile organic compounds (VOCs) especially larger aromatic species.

To obtain measurements on (as close to possible) the full suite of atmospheric volatile organic compounds, we have developed a method using comprehensive two dimensional gas chromatography coupled to a flame ionisation detector (GCxGC-FID). This is a high resolution method, with increased separation power and improved peak capacity when compared to many single column systems.<sup>2</sup> Air samples were collected at hourly intervals during the first field campaign of the ClearfLo project in Jan/Feb 2012. These air samples were analysed for C<sub>4</sub> to C<sub>12</sub> VOCs. The GCxGC-FID system has separated over 80 species (of which 22 have so far been identified), including oxygenates, aromatics, and saturated and unsaturated aliphatics. Including these extra VOCs should improve the prediction capability of air quality models.

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2. Lidster, R. T., Hamilton, J. F. and Lewis, A. C., *Journal of Separation Science*, 34, 812-821, 2011.

### 2. Field Measurements and Modelling Studies of Radicals during the ClearfLo Campaign

Noel Clancy and Dwayne E. Heard  
School of Chemistry, University of Leeds

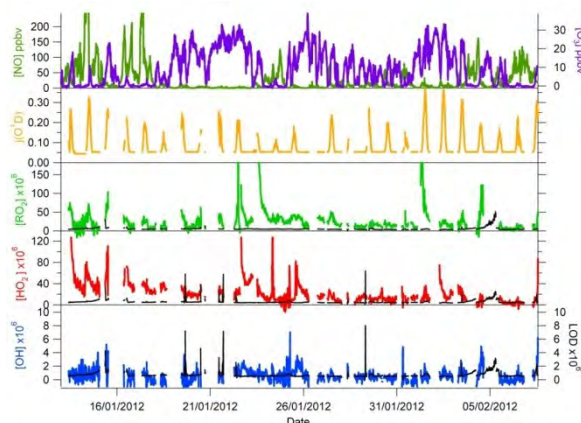
Urban air pollution endured in London and other large cities has adverse effects on human health. Current understanding of the processes responsible for London's poor air quality is incomplete, in large part because the photo-oxidation chem-

istry occurring in urban atmospheres is highly complex. This project aims to improve the accuracy with which atmospheric chemistry is parameterised within climate and air quality models by making detailed field measurements of atmospheric radicals ( $\text{OH}$ ,  $\text{HO}_2$  and  $\text{RO}_2$ ) in the London environment. Radicals initiate and propagate the oxidation cycles that remove harmful trace gases (e.g.  $\text{CO}$ , benzene) from the atmosphere.

Leeds University's ground-based FAGE instrument,<sup>1,2</sup> which uses laser-induced fluorescence (LIF) spectroscopy, has been deployed during the ClearfLo campaigns in London to quantify ambient hydroxyl ( $\text{OH}$ ) and hydroperoxy ( $\text{HO}_2$ ) radical concentrations. The instrument's measurement capabilities have also recently been extended to measure organic peroxy radicals ( $\text{RO}_2$ ). Radical measurements from the ClearfLo campaigns, such as those shown in **Figure 1**, are now being compared to calculations from a box model utilising the detailed *Master Chemical Mechanism*; this mechanism currently contains around 15,000 reactions and over 5,000 chemical species. The level of agreement between field measurements and models is an excellent test of how well we understand the fast production and loss of radicals in the atmosphere and their pivotal roles in the formation of secondary pollutants such as ozone.

1. Whalley, L. K., Heard, D. E., et al., *Atmospheric Chemistry Physics*, **11**, 7223, 2011.

2. Whalley, L. K., Heard, D. E., et al., *Atmospheric Chemistry Physics*, **10**, 1555, 2010.



**Figure 1:** Bottom three panels: Time series of  $\text{RO}_2$ ,  $\text{HO}_2$  and  $\text{OH}$  radical concentrations (in units of molecules/ $\text{cm}^3$ ) measured by the FAGE instrument during the first ClearfLo campaign 13<sup>th</sup> Jan – 7<sup>th</sup> Feb 2012. Top two panels: ancillary measurements of the concentrations of  $\text{NO}$  and  $\text{O}_3$ , and of the photolysis rate of ozone to produce electronically excited oxygen atoms,  $j(\text{O}^1\text{D})$ , which via their reaction with water vapour are the main source of  $\text{OH}$  radicals in the atmosphere.

### 3. Isoprene in the Remote Marine Boundary Layer

Sina C. Hackenberg, Lucy J. Carpenter and Alastair C. Lewis

Department of Chemistry, University of York

Oceanic organic carbon aerosol has been suggested to have a significant effect on climate through modification of the microphysical properties of low-level marine stratocumulus clouds.<sup>1</sup> Isoprene and monoterpenes (reactive volatile organic compounds emitted by phytoplankton) have been proposed to increase cloud albedo in the region of phytoplankton blooms due to the formation of such secondary organic aerosol.<sup>1,2</sup>

Several studies have shown that isoprene and monoterpene emissions vary depending on light, temperature, phytoplankton abundance and functional type.<sup>1</sup> However, the importance of isoprene and monoterpenes in the remote marine boundary layer is still unclear due to a lack of observations of its seasonal and diurnal variability, and the resulting uncertainties in model estimates of global oceanic emission fluxes.<sup>1</sup> Using existing and new measurements of isoprene and monoterpenes in marine air and seawater, this project investigates the relationships with meteorological and biological parameters in order to improve our understanding of the mechanisms and processes that control marine terpene emissions. The ultimate aim is to calculate new estimates of sea-air fluxes of these compounds.

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2. Meskhidze, N. and Nenes, A., *Science*, **314**, 1419, 2006.

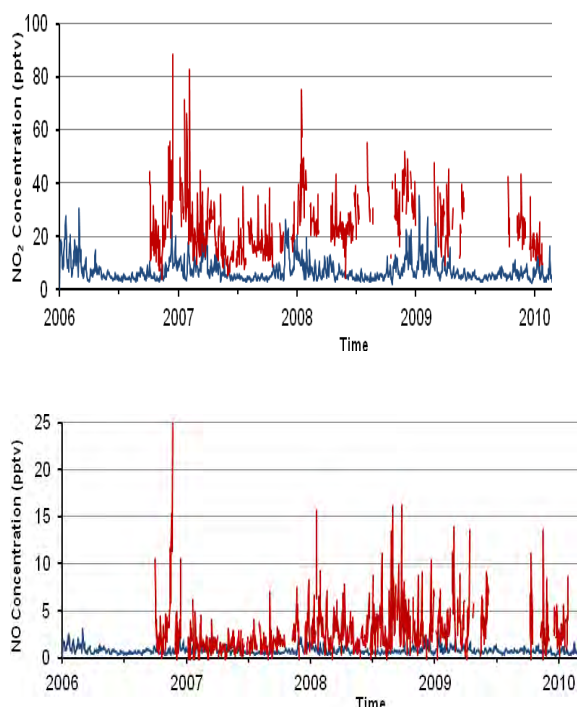
### 4. Speciated $\text{NO}_x$ Measurements in the Remote Tropical Troposphere at the Cape Verde Atmospheric Observatory (CVAO)

William D. Manning, James D. Lee and Lucy J. Carpenter  
Department of Chemistry, University of York

Trace quantities of nitrogen oxides ( $\text{NO} + \text{NO}_2 = \text{NO}_x$ ) affect the concentration of the hydroxyl radical and are precursors for the photochemical formation of tropospheric ozone ( $\text{O}_3$ ). The remote tropical troposphere is of special interest because  $\text{NO}_x$  levels are close to the critical mixing ratio at which the  $\text{O}_3$  destruction regime prevailing in “clean atmospheres” changes to one of photochemical  $\text{O}_3$  production. Oxidation of  $\text{NO}_x$  to longer-lived reservoir species ( $\text{NO}_2$ ), primarily peroxyacetyl nitrates (PANs), alkyl nitrates (ANs) and nitric acid ( $\text{HNO}_3$ ), allows nitrogen oxides to be transported over long distances; these reservoir species can then thermally decompose to release  $\text{NO}_x$  into remote environments, thereby resulting in perturbations to the local  $\text{O}_3$  regime. However, current global models have difficulty recreating both the magnitude and variability of  $\text{NO}_x$  concentrations in clean environments (for example, **Figure 2**), suggesting that

current understanding of the reactive nitrogen pool and its impacts on the remote tropical troposphere is incomplete.

The characteristic O-N bond energies of each species allow the sum of the reservoirs to be measured *via* thermal decomposition to yield  $\text{NO}_2$ , which is then detected by chemiluminescence (TD-Chem). The purpose of this work is to calibrate, install and operate a two-channel TD-Chem unit at the Cape Verde Atmospheric Observatory (CVAO) ( $16.848^\circ\text{N}$ ,  $24.871^\circ\text{W}$ ) in the equatorial Atlantic Ocean, capable of separately measuring  $\text{NO}$ ,  $\text{NO}_2$ , the sum of all peroxyacyl nitrates, the sum of all alkyl nitrates,  $\text{HNO}_3$  and total  $\text{NO}_y$  ( $= \text{NO}_x + \text{NO}_2$ ). These data will be used to improve the accuracy of atmospheric models and develop our understanding of this important class of atmospheric constituents.



**Figure 2:** Comparisons of the concentrations of nitrogen dioxide (top panel) and nitric oxide (bottom panel) measured at the Cape Verde Atmospheric Observatory since 1.10.2006 (red line) with the corresponding concentrations predicted by a GEOS model simulation since 1.1.2006 (blue line). The measurements exhibit higher concentrations and more variability than the model, potentially indicating more long-range transport of  $\text{NO}_x$  via reservoir compounds than is accounted for in the model.

## 5. Determination of the Atmospheric Loss Rates of $\text{NO}_3$ and $\text{N}_2\text{O}_5$ using Observational Data from the RONOCO Campaign

M. McLeod, B. Ouyang and R. L. Jones,  
Department of Chemistry, University of Cambridge

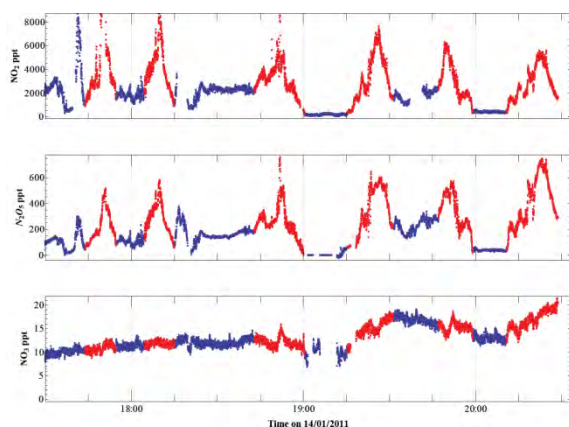
During the day, the OH radical acts as the dominant species driving oxidation chemistry in the troposphere (the lowermost atmospheric layer). But because there can be no photochemical production of OH radicals at night, another oxidant species, the nitrate radical ( $\text{NO}_3$ ), takes over the role of initiating night-time oxidative reactions.<sup>1</sup>  $\text{NO}_3$  is in thermal equilibrium with  $\text{N}_2\text{O}_5$  and both species can establish significant concentrations at night. As well as potentially affecting ozone budgets *via* their night-time chemistry, physical and/or chemical removal of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  also acts as an important sink for removing  $\text{NO}_x$  from the atmosphere.<sup>2</sup> The aim of the RONOCO (ROle of Night-time chemistry in controlling the Oxidising Capacity of the atmOsphere) campaign was to quantify the processes influencing night-time chemistry over the UK and near-continental Europe using a combination of airborne measurements and atmospheric modelling on different scales.

The RONOCO consortium comprised research groups from the Universities of Cambridge, East Anglia, Leicester, Leeds, Manchester and York. Measurements, including  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{NO}_x$ ,  $\text{O}_3$ , CO, aerosol,  $\text{HNO}_3$ , peroxy alkyl nitrates and volatile organic compounds, were taken from on-board the FAAM (Facility for Airborne Atmospheric Measurements) BAe-146 research aircraft during flights around the UK in July-August 2010 and January 2011. A total of ninety flying hours were completed. Here we present  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_2$  measurements made with a new three channel broadband cavity enhanced absorption spectroscopy instrument.<sup>3</sup> Figure 3 shows an example of measurements taken on one flight during the January 2011 campaign. In this presentation, we explore different methods by which the rate constants for direct chemical loss of  $\text{NO}_3$  and the aerosol uptake coefficient of  $\text{N}_2\text{O}_5$  can be derived. We also investigate how to appropriately partition the total sink of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  between the individual loss processes under the different chemical environments experienced during the RONOCO campaign.

1. Brown, S. S. and Stutz, J., *Chemical Society Reviews*, **41**, 6405, 2012.

2. Chang, W. L., Bhave, P. V., Brown, S. S., et al., *Aerosol Science and Technology*, **45**, 665, 2011.

3. Kennedy, O. J., Ouyang, B., Langridge, J. M., Daniels, M. J. S., Bauguutte, S., Freshwater, R., McLeod, M. W., Ironmonger, C., Sendall, J., Norris, O., Nightingale, R., Ball, S. M., Jones, R. L., *Atmospheric Measurement Techniques*, **4**, 1759, 2011.



**Figure 3:** Time series of  $\text{NO}_2$ ,  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  concentrations recorded on a winter flight over the North Sea, starting 90 minutes after sunset. Highlighted in red are several transects across the same pollution plume originating from the Liverpool and Manchester urban areas. Each transect is further down-stream of the source; the  $\text{N}_2\text{O}_5$  concentrations increase on each transect, showing how night-time chemistry within the plume evolves, converting  $\text{NO}_2$  into  $\text{N}_2\text{O}_5$ .

## 6. Comparison of Reactive Gas Emissions from Bioenergy and Arable Crops

E. C. Morrison<sup>1,2</sup>, M. R. Heal<sup>1</sup> and J. Drewer<sup>2</sup>

<sup>1</sup> School of Chemistry, University of Edinburgh

<sup>2</sup> Centre for Ecology and Hydrology, Penicuik, Edinburgh

Depletion of fossil fuel resources, pollution concerns and the challenge of energy security are driving the search for renewable energy sources. Around 7% of all UK arable land (~1.3 M ha) may be planted with bioenergy crops by 2020 in order to meet renewable energy and  $\text{CO}_2$  reduction targets. Although bioenergy crops are perceived as ‘carbon neutral’, changes in land use can have a wider impact on atmospheric composition than through their  $\text{CO}_2$  emissions alone. This study compares vegetation fluxes of methyl halides and volatile organic compounds (VOCs) from adjacent bioenergy and arable crops. Methyl halide gases impact on levels of stratospheric ozone, whilst VOCs affect atmospheric oxidising capacity and cause the formation of tropospheric ozone and secondary organic aerosols. There are very few previous measurements of these reactive gases from bioenergy crops.

All fluxes measured demonstrate a strong seasonal trend with higher emissions occurring during growing season and low to zero emissions over winter. A diurnal pattern of high emissions during the day and low to zero emissions at night is also seen. These are the first reported measurements of methyl halides from bioenergy crops. The highest fluxes for both  $\text{CH}_3\text{Br}$  and  $\text{CH}_3\text{Cl}$  were produced by oilseed rape. Standardised emission rates of isoprene from willow of 0.01–1 ng per gramme dry weight per hour have previously been re-

ported, but our measurements indicate that the real figure could be much higher.

*Brassica* species such as oilseed rape are known to be high emitters of  $\text{CH}_3\text{Br}$ , as corroborated by these measurements; therefore extensive planting whether for food or fuel is likely to contribute to ozone layer destruction. High isoprene emissions from willow mean that increased planting, coupled with a warming climate, could have a considerable effect on atmospheric composition.

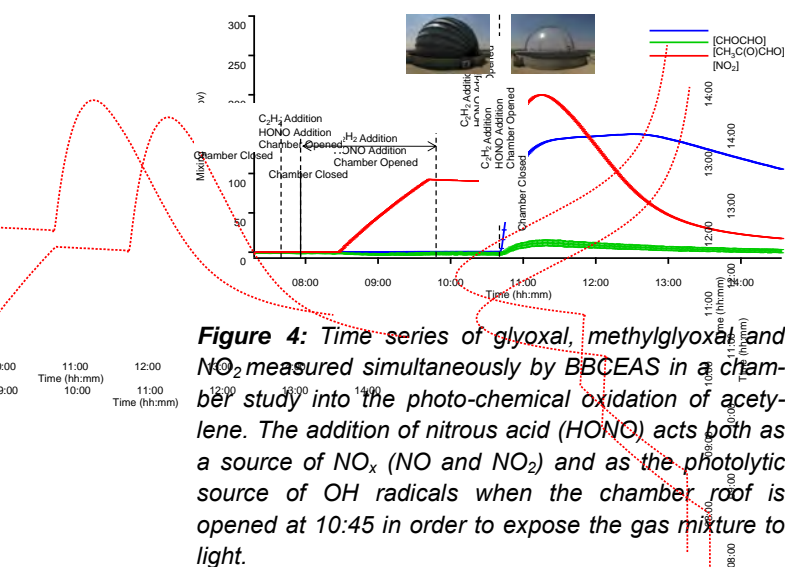
## Section 2: New and emerging Instrumentation

### 7. Detection and Quantification of Glyoxal, Methylglyoxal and $\text{NO}_2$ by BBCEAS

Thomas J. Adams, Mark J. S. Daniels and Stephen M. Ball  
Department of Chemistry, University of Leicester

Glyoxal ( $\text{CHOCHO}$ ) and methylglyoxal ( $\text{CH}_3\text{C(O)CHO}$ ) are common intermediates formed in the OH initiated photo-oxidation of a wide range of volatile organic compounds (VOCs) emitted from both anthropogenic and biogenic sources.<sup>1</sup> Such  $\alpha$ -dicarbonyl compounds have been reported as potential precursors of secondary organic aerosol (SOA), and therefore may account for a proportion of the SOA currently missing from atmospheric models.<sup>2</sup>  $\text{NO}_2$  is emitted primarily through the burning of fuels and has a significant role in the chemistry of the urban air quality: the catalytic photochemical cycling of  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) is the major source of ozone in the troposphere. As well as being a respiratory irritant, ozone plays a significant role in the chemical processing of reactive trace gases in the lower atmosphere.

Broadband Cavity Enhanced Absorption Spectroscopy (BBCEAS) is a highly sensitive absorption spectroscopic technique that has been applied to detect and quantify trace gases in the atmosphere and in atmospheric simulation chambers.<sup>3</sup> Gases are sampled into the instrument and into an optical cavity constructed between two highly reflective mirrors. The effective path length of the absorption measurement is increased typically several thousand-fold through multiple reflections of light inside the cavity, thereby enabling target compounds to be quantified at sub-parts-per-billion concentrations. Molecules are identified by their absorption features at characteristic wavelengths and concentrations retrieved through fitting absorption features with reference absorption cross sections. **Figure 4** shows an example of simultaneous glyoxal, methylglyoxal and  $\text{NO}_2$  measurements from recent experiments at the EUPHORE atmospheric chamber in Valencia (Spain) aimed at quantifying glyoxal and methylglyoxal yields from the photochemical oxidation of unsaturated volatile organic compounds.



**Figure 4:** Time series of glyoxal, methylglyoxal and  $\text{NO}_2$  measured simultaneously by BBCEAS in a chamber study into the photo-chemical oxidation of acetylene. The addition of nitrous acid (HONO) acts both as a source of  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) and as the photolytic source of  $\text{OH}$  radicals when the chamber roof is opened at 10:45 in order to expose the gas mixture to light.

1. Calvert, J. G., Atkinson, R., Becker, K. H., Kamens, R. M., Seinfeld, J. H., Wallington, T. J., and Yarwood, G., *The Mechanisms of Atmospheric Oxidation of Aromatic Hydrocarbons*, Oxford Univ. Press, 2002.
2. Fu, T.-M., Jacob, D. J., Wittrock, F., Burrows, J. P., Vrekoussis, M., and Henze, D. K., *Journal of Geophysical Research*, **113**, D15303, 2008
3. Ball, S. M., Langridge, J. M., and Jones, R. L., *Chemical Physics Letters*, **398**, 68, 2004

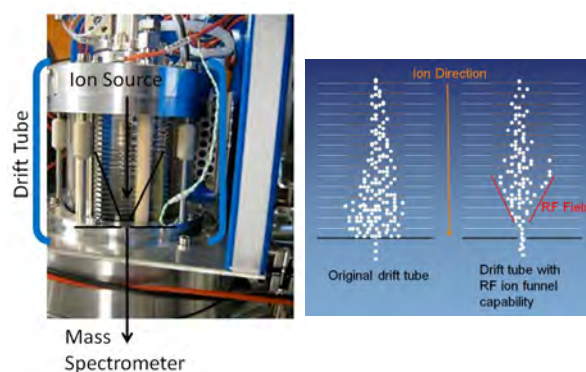
## 8. Increased Sensitivity in Proton Transfer Reaction Mass Spectrometry by Incorporation of a Radio Frequency Ion Funnel

Shane Barber<sup>1</sup>, Robert S. Blake<sup>1</sup>, Iain R. White<sup>1</sup>, Paul S. Monks<sup>1</sup>, Fraser Reich<sup>2</sup>, Steve Mullock<sup>2</sup> and Andrew M. Ellis<sup>1</sup>  
<sup>1</sup>Department of Chemistry, University of Leicester  
<sup>2</sup>Kore Technology Limited, Cambridgeshire Business Park, Ely, Cambridgeshire.

Proton Transfer Reaction-Time of Flight-Mass Spectrometry (PTR-ToF-MS) has proven itself a versatile technique capable of measuring a wide range of trace volatile organic compounds (VOCs) and oxygenated volatile organic compounds (OVOCs). Its applications are varied, ranging from both indoor and outdoor atmospheric chemistry to the medical and forensic sciences.<sup>1</sup> In contrast to more conventional forms of mass spectrometry, PTR-ToF-MS captures data from all mass channels within a potentially complex gas mixture, simultaneously and in real time. This allows VOCs to be detected *in situ*, whether the measurements are performed in the laboratory, hospital or in the field.

A drift tube that doubles as an ion funnel is demonstrated in proton transfer reaction mass spectrometry for the first time. The ion funnel enables a much higher proportion of

( $\text{VOC}+\text{H}$ )<sup>+</sup> product ions to exit the drift tube and enter the mass spectrometer than would otherwise be the case (see **Figure 5**). A large increase in the detection sensitivity for volatile organic compounds of between one and two orders of magnitude is delivered, and has been characterized against dilution standards for a range of compounds. The improvements in both sensitivity and limit of detection allow this instrument to now detect a wider range of VOCs at a lower concentration. The instrument is currently being applied to quantify ambient VOC concentrations in order to help better understand atmospheric processes.



**Figure 5:** A photograph of the PTR-ToF-MS drift tube doubling as an ion funnel (left). "Before and after" schematics of the ion funnel (right) the showing altered radio-frequency electric field inside the drift tube, and how the RF field guides ions through the orifice into the mass spectrometer.

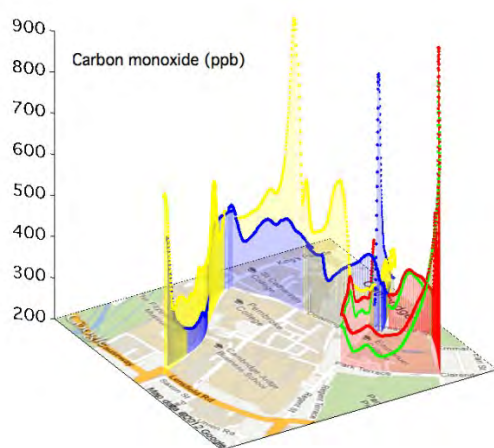
1. Barber S., Blake R. S., White I. R., Monks P. S., Reich F., Mullock S., Ellis A. M., *Analytical Chemistry*, **84**, 5387, 2012.

## 9. Sensor Networks for Air Quality

V. B. Bright<sup>1</sup>, M. I. Mead<sup>1</sup>, O. A. M. Popoola<sup>1</sup>, R. P. Baron<sup>2</sup>, J. R. Saffell<sup>2</sup>, G. B. Stewart<sup>1</sup> and R. L. Jones<sup>1</sup>  
<sup>1</sup> Department of Chemistry, University of Cambridge  
<sup>2</sup> Alphasense, Sensor Technology House, Great Notley

The ability of low-cost, portable devices that incorporate electrochemical sensors to measure gases such as  $\text{CO}$ ,  $\text{NO}$  and  $\text{NO}_2$  at ambient concentrations has been demonstrated during deployments in urban areas including London, Valencia, Kuala Lumpur and Lagos. The sensors additionally include GPS (Global Positioning System) and GPRS (General Packet Radio Service) for positioning and data transmission, respectively. Laboratory tests carried out against gas standards at the parts-per-billion level have demonstrated the high sensitivity and linear response of electrochemical sensors to their respective target gases. Moreover, when such sensors are co-located with reference instruments in the field, they have shown a high level of agreement.<sup>1</sup>

The degree of variability in pollutant levels, on both spatial and temporal scales, has been highlighted in various mobile sensor campaigns. An example of mobile carbon monoxide measurements around central Cambridge is shown in **Figure 6**. Such measurements also highlight the limitations of a sparsely populated static urban network that would fail to capture the highly variable concentration fields evident in **Figure 6**. Thus the technology outlined here has been extended to establish a dense, urban network of autonomous, static units capable of capturing data with high temporal resolution over a period of several months. The results of such deployments highlight the importance of meteorology, traffic and street canyon characteristics in determining the level of pollutants observed. In this presentation we show initial observations of NO, NO<sub>2</sub>, CO, CO<sub>2</sub>, SO<sub>2</sub>, O<sub>3</sub>, volatile organic compounds, size-specified particulate matter and meteorological variables obtained using a high-density network of air quality sensors deployed in and around London Heathrow airport.



**Figure 6:** Selected CO measurements from two sensor nodes in parts of central Cambridge superposed on a road map. Data from periods when the volunteers carrying the sensors were walking together are shown in red and green, and those from when they walked apart are shown in yellow and blue.<sup>1</sup>

1. M. I. Mead, O.A.M. Popoola, G. B. Stewart, P. Landshoff, M. Calleja, M. Hayes, J. J. Baldovi, M. W. McLeod, T. F. Hodgson, J. Dicks, A. Lewis, J. Cohen, R. Baron, J. R. Saffell and R. L. Jones, *submitted to Atmospheric Environment*, 2012.

#### 10. A New System for Measuring Ozone Production Rates

Hao Huang, William Bloss, Kate Faloon and Juan Najera  
School of Geography, Earth and Environmental Science,  
University of Birmingham

Ground level ozone is harmful to humans, vegetation and the environment, and is considered one of the principal air

pollutants. In order to develop effective air quality policies to reduce ambient O<sub>3</sub> concentrations, it is important to understand ozone production processes, and specifically the chemical ozone production rate, in order that this may be related to primary emissions. A direct ozone production rate measurement (“OPR method”) provides a new way to monitor *in situ* chemical ozone formation, complementing traditional modelling approaches.<sup>1</sup> The principle of the OPR system is to sample air into two parallel reactors; ambient chemical processing occurs as normal in one reactor (the sample reactor), whilst in the other the radical chemistry is suppressed (the reference reactor). The difference in ozone levels exiting the reactors, after correction for NO<sub>x</sub> photochemical steady state perturbation, determines the *in situ* ozone production rate. The design and initial deployment of a prototype OPR system is described, and future applications of the measurements are considered.

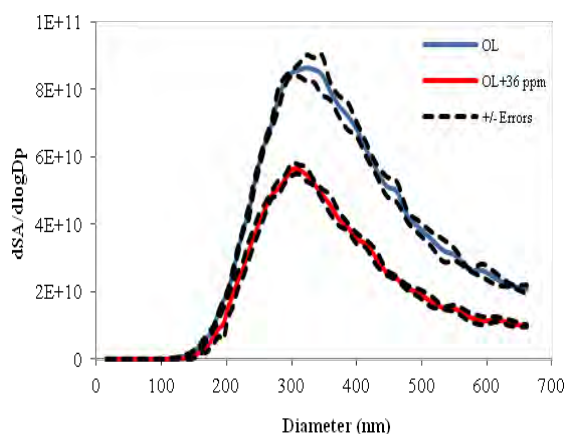
1. Cazorla, M., Brune, W. H., Ren, X., and Lefer, B., *Atmospheric Chemistry and Physics*, **12**, 1203, 2012.

### Section 3: Aerosol and particulate matter

#### 11. Artificial Chemical Ageing of Ambient Atmospheric Aerosol

S. S. Al Kindi, R. M. Harrison and W. J. Bloss  
School of Geography, Earth and Environmental Sciences,  
University of Birmingham

Atmospheric aerosol play critical roles in air quality, visibility, human health, regional and global climate, the ability to act as cloud condensation nuclei, precipitation events, atmospheric acid deposition, optical properties, atmospheric energy balance, and stratospheric ozone depletion.<sup>1</sup> Field measurements and air quality models have shown limitations in our understanding of the heterogeneous reactions and processing of aerosol-associated organic matter.<sup>2</sup> An experimental system for the artificial chemical ageing of atmospheric aerosol particles is described, and initial results from the processing of laboratory-generated oleic acid particles are presented. Within the apparatus, gas phase oxidant levels are maintained several orders of magnitude above ambient levels (e.g. [OH] = 0.5–2 × 10<sup>10</sup> molecule cm<sup>-3</sup> and [O<sub>3</sub>] = 1–50 ppm) such that atmospheric exposures equivalent to several days or weeks may be achieved in minutes in the laboratory (subject to limitations relating to particle mass transfer and diffusion). **Figure 7** shows an example of the size distributions of oleic acid aerosol particles before and after processing by 36 parts per million of ozone. Measurements of the physical properties of processed aerosol particles are accomplished by a Scanning Mobility Particle Spectrometer (SMPS), while the chemical content of the particles is monitored by an Aerosol Time of Flight Mass Spectrometer (ATOFMS). The aim is to apply the technique to ambient atmospheric particles in order to assess their chemical evolution.



**Figure 7:** A comparison of size distributions for pure (unprocessed) oleic acid aerosol particles (blue), and their equivalent after exposure to 36 ppm of ozone (red). Dashed lines indicate the measurement uncertainty ( $\pm 1\sigma$  precision).

1. Kolb, C. E. and Worsnop, D. R., *Annual Review of Physical Chemistry*, **63**, 471, 2012.
2. Simon, H. and Bhawe, P. V., *Environmental Science & Technology*, **46**, 331, 2012.

## 12. Bioaccessibility of the Inhalable Fractions of Urban Road Dust

Andrew Brown<sup>1</sup>, Sanja Potgieter-Vermaak<sup>1,2</sup>, Judith Barret<sup>1</sup> and Rene Van Grieken<sup>3</sup>

<sup>1</sup>Division of Chemistry & Environmental Science, Manchester Metropolitan University.

<sup>2</sup>School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.

<sup>3</sup>Department of Chemistry, University of Antwerp, Belgium.

*In vitro* and animal toxicological studies have confirmed that the chemical composition of inhaled particles play a major role in their toxic, genotoxic and carcinogenic mechanisms, but the component-specific toxic effects are still not understood. Particle-bound airborne transition metals can also lead to the production of Reactive Oxygen Species in lung tissue; a special concern amongst particularly susceptible cohorts (children and elderly). Thus the bioaccessibility of the fine fraction aerosol is evidently of importance for public health.

Size-fractionated (<38, 38–63, 63–125  $\mu\text{m}$ ) road dust samples collected from one of the highest trafficked roads in the United Kingdom (and believed to be one of the busiest bus routes in Europe) were characterised for their bulk elemental composition with EDXRF, ICP-OES and ICP-MS, and their molecular composition with micro Raman spectroscopy (MRS). It was found that the fine fraction (<38  $\mu\text{m}$ ) had the highest Pb (238 ppm) and Cr (171 ppm) concentrations. Concentrations of both Pb and Cr decreased substantially in

the largest particle size fractions (from 279 ppm in particles with diameters  $D_p < 38 \mu\text{m}$  to 13 ppm in particles with  $D_p < 1\text{mm}$  for lead; and from 171 ppm for  $D_p < 38 \mu\text{m}$  to 91 ppm for  $D_p < 1\text{mm}$  for chromium). The MRS data showed that the Cr was mostly present as lead chromate and therefore in the Cr(VI) oxidation state. Apart from rather alarmingly high concentrations of oxidative stressors (Cu, Fe, Mn) obtained from the elemental analysis, the carcinogenic potential of the respirable fraction is evident from the MRS data. These same fractions underwent *in vitro* testing to assess the mobility of toxic and carcinogenic components by leaching with artificial body fluids. Leachates were analysed for Cr, Cu, Zn, V, Pb, Mn, Cd, Fe, Ni, Al and As concentrations at time intervals from 1 hour to 8 weeks. In general, most of the elements leached in the ppb range and concentrations decreased with increasing particle size. Although the mobility in the artificial body fluids of the various elements varied, up to 19% Cr, 47% Pb and 87% Ni were released.

## 13. Improving the Modeling of Bioaerosol Dispersion from Green Waste Composting Facilities

Philippa Douglas<sup>1</sup>, Gillian Drew<sup>1</sup>, Rob Kinnersley<sup>2</sup>, Kerry Walsh<sup>2</sup>, Phil Longhurst<sup>1</sup> and Sean Tyrrel<sup>1</sup>

<sup>1</sup>Centre for Energy and Resource Technology, School of Applied Sciences, Cranfield University

<sup>2</sup>Environment Agency, Olton, Solihull

The potential adverse effects on human health posed by exposure to bioaerosols emitted from composting facilities is a growing concern, particularly as more waste is being diverted from landfill.<sup>1</sup> At present, site monitoring is carried out using filtration or impaction samplers,<sup>2</sup> but this only provides a snapshot of emissions in space and time. Dispersion models could play a valuable, complementary role to bioaerosol monitoring by providing a more continual overview of bioaerosol concentrations under different meteorological and operational scenarios. However, only modest progress has been made to date when applying a dispersion model in this context<sup>3</sup> and currently there is a lack of confidence in our ability to deploy atmospheric dispersion models to predict the dispersion of bioaerosols emitted from composting facilities.

Previous research has found that bioaerosol concentrations are underestimated when using the ADMS dispersion model.<sup>3</sup> It is suggested that this is mainly due to lack of detailed characterisation of the source term, and uncertainties regarding how to represent this type of scenario in the dispersion model. A detailed scenario-specific sensitivity analysis is necessary to identify the significant model input parameters to commence model optimization and validation. Alongside this, source data collection, which has also been recognised as a contributor to model underestimations, is needed to initiate modelling improvements.

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3. Drew, G. H., Tamer Vestlund, A. T., Jordinson, G., Taha, M. P. M., Smith, R., Tyrrel, S., Longhurst, P. J., and Pollard, S. J. T., *In: Proceedings Sardinia 2007, Eleventh International waste management and landfill symposium. CISA, Environmental Sanitary Engineering Centre, Italy*, 2007.

#### 14. Characterization of Personal Exposures to and Indoor Concentrations of VOCs, PM<sub>2.5</sub>, PAHs, Quinones and Black Carbon

B. A. Macias-Hernandez, J. M. Delgado-Saborit and R. M. Harrison

School of Geography, Earth and Environmental Sciences, University of Birmingham.

There is growing public awareness regarding the risks associated with poor indoor air quality in the home and workplace.<sup>1,2</sup> The aim of this study is to measure personal exposures in indoor environments and to estimate the lung doses of several pollutants of interest. Forty-five healthy, non-smoking adult subjects will be recruited, selected according to their likely different exposures to organic pollutants. The volunteers are grouped, for example, into (i) subjects occupationally exposed to benzene, (ii) subjects living or working in new buildings, and (iii) a control group. Volunteers are requested to carry a briefcase containing sampling equipment for a period of 24 hours and to complete time-activity diaries.

A total of 46 filters were sampled from the first group of 16 volunteers recruited during winter 2011. Marginally higher concentrations of PM<sub>2.5</sub> (particulate matter with diameters  $\leq 2.5 \mu\text{m}$ ) were found in the workplace, with an arithmetic mean of  $30 \pm 15 \mu\text{g}/\text{m}^3$ . These values are generally higher than the standard proposed by the World Health Organization ( $25 \mu\text{g}/\text{m}^3$ ).<sup>3</sup> Results from a total of 4,455 observations (sampling time of 5 minutes each) showed that the highest concentrations of black carbon were found outdoors ( $5,163 \pm 3,121 \text{ ng}/\text{m}^3$ ), whilst the highest concentrations measured indoors were in pubs and restaurants ( $2,901 \pm 4,229 \text{ ng}/\text{m}^3$ ).

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#### 15. Assessment of Vehicular Profiles vis-à-vis Real-world Traffic Emissions

Pallavi Pant and Roy M. Harrison

School of Geography, Earth and Environmental Studies, University of Birmingham

Receptor modelling, particularly the chemical mass balance (CMB) model is one of the often-used tools for estimation of source contributions to concentrations of particulate matter in ambient air. Further, the CMB model relies to a large extent on the accuracy of the source profiles used as an input. Most gasoline and diesel engine source profiles are generated through emission characterizations performed under laboratory conditions. However, significant differences have been observed between laboratory-testing and real-world mixed source traffic emissions.<sup>1,2</sup>

To achieve the twin goals of assessing existing source profiles with respect to the ambient traffic emissions data and preparation of a mixed-source traffic profile for London, samples were collected at two different urban sites (background and roadside) in London. It was assumed that if all other sources contribute to the same extent at both sites, the increment in marker concentrations would be due to traffic emissions. Ambient organic marker data from London was compared with published source profiles using ratio-ratio plots. Results indicate that mixed-traffic profiles generated using data collected from the ambient environment show a greater similarity with ambient concentrations. This can be attributed to the relative similarity to the real-world driving and emission conditions. Also, while the lab-generated source profiles vary significantly from each other in some cases, most of the real-world profiles show high levels of similarity. A local traffic emissions profile has also been prepared for London which is being used for further data analysis.

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#### Section 4: Environmental electrochemistry

##### 16. Investigation of the Uranium Redox Couple by Voltammetric Techniques

Mei Qi CHEW, Nick D. M. Evans and Roger J. Mortimer  
Department of Chemistry, University of Loughborough

Uranium is a redox-sensitive element and its chemical properties depend considerably on pH and oxidation state. This work is concerned with the oxidation-reduction behaviour of uranium in a potential radioactive Geological Disposal Facil-

ity (GDF). It is important to understand the redox behaviour of uranium in order to evaluate its mobility in the GDF environment and the consequent security of its disposal. The low solubility of uranium at high pH makes conventional experimental voltammetric techniques difficult to use. The main aim of this work is therefore to investigate the chemical effects (pH, addition of chelating agents *etc*) on the behaviour of the uranium couple and optimise the cyclic voltammetric technique.<sup>1,2</sup>

This work describes the effect of changing pH on the redox behaviour and the reversibility of the various uranium redox couples using voltammetric techniques and optimisation of the method. Cyclic voltammetry did not produce satisfactory results at low concentrations of uranium ( $\sim 10^{-5}$  mol dm<sup>-3</sup>). The concentrations of uranium were then increased to the mM range and subsequently more defined and reproducible voltammetric waves were obtained.

Experiments were performed using uranyl nitrate across a pH range from 1 to 14 in the presence and absence of sodium carbonate.<sup>2</sup> The kinetic effects, mechanisms and thermodynamics of the redox reactions were investigated. The effects of the addition of ethylenediaminetetraacetic acid (EDTA) were subsequently studied, and the electrode potentials of the redox couple in non-ligand and ligand systems were compared. The effects of organic complex formation on the redox behaviour of the uranium couple were also observed.

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**ABSTRACTS WERE PROVIDED BY THE FORUM DELEGATES. EDITING BY STEPHEN BALL and WILLIAM BLOSS**

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## The World Meteorological Organization's provisional annual statement on the state of global climate in 2012

Last year (2012) saw record arctic sea ice melt, multiple weather extremes, and high temperatures, according to the World Meteorological Organization (WMO). The WMO's provisional annual statement on the state of the global climate, released at the end of November 2012 to inform negotiators at the United Nations Climate Change Conference in Doha, Qatar, shows that despite the cooling influence of La Niña early in the year, January to October 2012 were the ninth warmest such period since records began in 1850.

A particularly worrying trend is the decline in Arctic Sea Ice. In August 2012, the fastest loss for this month on record was recorded. By 26 August, sea ice extent had

dropped below the previously observed minimum extent, set on 18 September 2007. According to the statement, "The Arctic reached its lowest sea ice extent in its annual cycle on record on September 18<sup>th</sup>, at 3.41 million square kilometres. This value broke the previous record low set on September 18<sup>th</sup>, 2007 by 18 percent and was 49 percent [...] below the 1979-2000 average minimum."

The statement also summarizes the latest analysis of observations from the WMO Global Atmosphere Watch (GAW) regarding the state of greenhouse gases in the atmosphere. Carbon dioxide, methane, and nitrous oxide concentrations in the atmosphere reached new highs, with the carbon dioxide concentration reaching  $390.9 \pm 0.1$  parts per million.

Final updates and figures for 2012 will be published in March 2013.

For the complete statement, see: [http://www.wmo.int/pages/mediacentre/press\\_releases/documents/966\\_WMOstatement.pdf](http://www.wmo.int/pages/mediacentre/press_releases/documents/966_WMOstatement.pdf)

The latest WMO Greenhouse Gas Bulletin can be found at <http://www.wmo.int/pages/prog/arep/gaw/ghg/GHGbulletin.html>



Annette Holmberg/Shutterstock

## Forthcoming symposium

### The history of the chemical industry in the Runcorn–Widnes area

#### Organised by the RSC Historical Group

**Where:** Catalyst Museum and Science Discovery Centre, Mersey Road, Widnes, Cheshire, WA8 0DF

**When:** Saturday March 2nd, 2013

#### Programme

10.15 Coffee and tea

10.45 Welcome

10.50 **Dr John Beacham**, CBE, DSc: Runcorn's Chemical Foundation, or Location, Location, Location

11.30 **Dr John Hudson**, FRSC: Leblanc Widnes

12.10 LUNCH

13.25 **Peter Reed**, Independent Researcher: "Widnes: Where's there's muck, there's brass!"

14.00 Launch of book by **Gerald Hayes**, MRSC: The Catalyst Triangle - Mathieson, McKechnie and Wigg.

14.10 **Diana Leitch**, FRSC: Runcorn and Widnes in the first half of the 20th century

14.55 **Dr Vincent Attwood**, MInstP: Nuclear Bomb Work at Runcorn during WW2

15.15 TEA

15.35 **Prof. Colin Suckling**, OBE, DSc, FRSE: The Latter Days of the Widnes Research Laboratory.

16.05 **Dr Jenny Clucas**, MRSC: Runcorn and Widnes – the future

16.45 Closing remarks and close of meeting

There is ample free parking at Catalyst. See here for directions. Nearest station is Runcorn; walk over the bridge or take a taxi. A convenient train departs Euston 0807, arrives 0955.

#### REGISTRATION FORM

**Advance registration and pre-payment is essential.** I wish to attend the RSCHG- Meeting *The History of the Chemical industry in the Runcorn – Widnes Area* and enclose a cheque for £15, payable to the RSC Historical Group. This charge includes a sandwich lunch morning and afternoon tea or coffee.

Name..... e-mail.....

Address (please print).....

..... (postcode).....

To register, please return the above form with a cheque for £15, payable to 'RSC Historical Group' to Dr. John Hudson, Graythwaite, Loweswater, Cockermouth, Cumbria CA13 0SU. Receipt of cheques will be acknowledged to applicants who give their e-mail address. For any problems or queries please contact John Hudson at [johnhudson25@hotmail.com](mailto:johnhudson25@hotmail.com).

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