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Environmental Chemistry Group

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Bulletin

The impacts and regulation of pesticides and other chemicals were the focus of a joint RSC ECG ±Toxicology Group meeting on 7KH /HJDF\ RI 5DFKHO &DUVRQ held in October 2012 to commemorate the 50th anniversary of the publication of 6LOHQW 6SULQJ. 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 SUREOHP RI µZDVWH¶ LQ WKH 8.¶V current post-industrial revolution landscape compared with its Victorian past. The disposal of waste from the Leblanc alkali industry in the 19th century affected the health of local populations and degraded the landscape. By contrast, the recycling of organic waste in the 21

Contents

ECG ***Bulletin***

Published biannually by the 5 R \ D O 6 RF&LKHPLV\ W U \ ¶ V (RSC) Environmental Chemistry Group (ECG), Burlington House, Piccadilly, London, W1J

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 ñFuel, Chemicals and Materials from Wasteò.

In - X ,Q 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 38- a358

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 RSCôs Environment, Sustainability and Energy Division.

The aim of the meeting was to present a number of perspectives on how Rachel Carsonôs 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).

The meeting began with Professor Andy Smith (MRC, Leicester) giving a brief history of Rachel Carsonôs 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 years of toxicological risk assessmentò (see pp 7-9 for Dr Rodricksô 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 20th century, and the 1906 Pure Food and Drug Act, which declared that food and drugs shall not contain adulterants that ñmay cause harm.ò This Act led to the use of animal studies to characterise the effects of harm. Other pre-Silent Springdrivers 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 re 4TJ T* [(2)18(il)-3(se)4(-3(u)7(ti)e)4(41(w)a)4(t)fut(v)7((m))-189(t(0-189TJ T* 009(r(a)4(s)- 64se)4(-3
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A century of extraordinary progress in the worlds of pure and applied chemistry was, with the publication in 1962 of Rachel Carsonôs 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.[1,2] 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.[2] 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.[3]

The problem of identifying safe levels of human exposure to chemicals exhibiting toxicity (which virtually all chemicals will do at suf( )-216(p)-6(7c)-29(o)-6(f)13oox f Td (.)s o46 043(e)-8(m)18(ica)6(-3(f-3(edDC T* [(c)7c)-29(o)-6(f)P <</MCID 9 e-6(f)

assessments should inform decision-making. Another study by the National Research Council, issued in 2009 under the title Science and Decisions: Advancing Risk Assessment,[10] 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

RSC Environmental Chemistry Group

2013 ECG Distinguished Guest Lecture & Symposium Rare earths and other scarce metals: Technologically vital but usually thrown away

20th March 2013, Royal Society of Chemistry, Burlington House, London

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 ECGïToxicology Group meeting, which was held in September to celebrate the 50th anniversary of the publication of Rachel Carsonôs influential book, Silent Spring

The RSCôs 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 acroRS4elds9(im)1-40(h)-6(u)-6(p)-6Exm app

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 ï 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 ï formed from alkene ozonolysis ï 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 SF_6^- and I^- reagents, for the detection of organic acids in the atmosphere, and concluded by introducing a new potential ñuniversalò 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 discussed1u12 Td [(sity)12(w)15(h)-6(ic7(r)-29((iv)5 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. Fraserôs talk described the process from initial idea, through design & testing iterations, until finally the ñlight at the end of the funnelò (his words) was reached, with sensitivity increases of 1ï 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 characterising emissions from Mangoes during their ripening process (with apparently significant value for maximising the efficiency of supply lines) to forensic investigations and medical uses ï the potential for exhaled breath analyses to provide non-invasive screening and/or diagnostic tests. Paulôs 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.

As an outcome of the meeting, it has been suggested that a new ñSoft Ionisation Mass Spectrometry Users Groupò 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

WILLIAM BLOSS

References

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

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 25th 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 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.[1]

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.[2] As an integral part of its function, AQEG conforms to the government principles of scientific advice.[3] 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 mandate 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.[4] 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

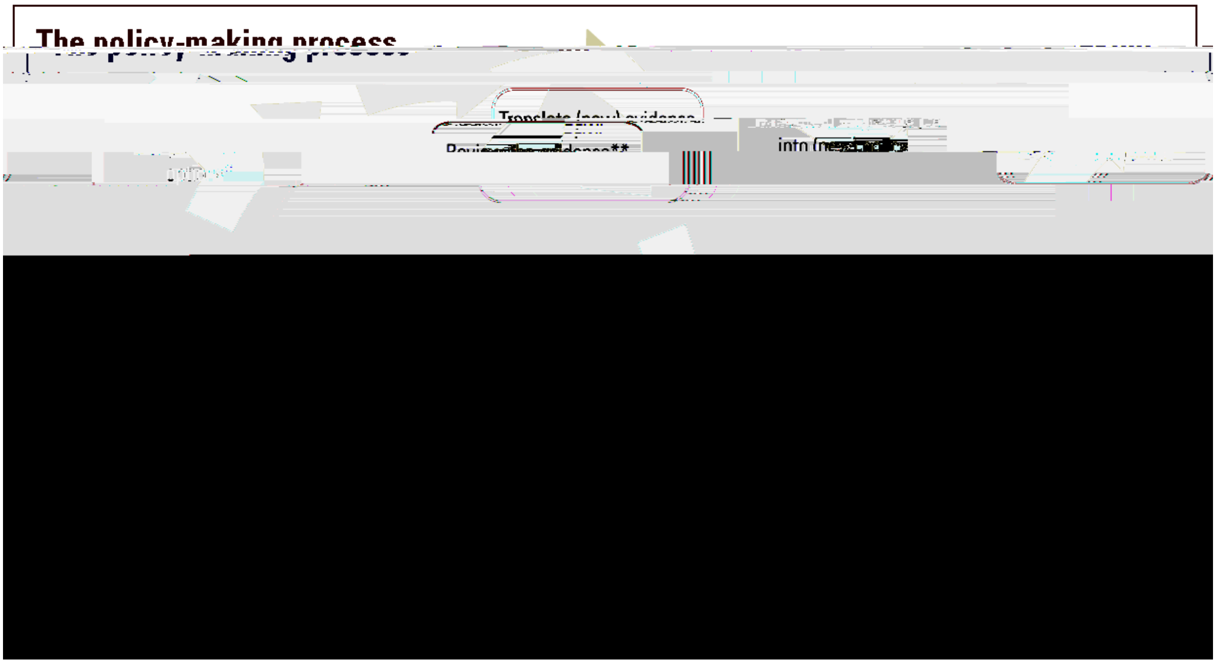

Figure 1: 7KH SROLF\ PDNLQJ SURFHVV DQG RSSRUWXQLWLHV IRU VFLHQ[7]

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 ñtraditionalò 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 routin(e)4( )-1700550003>4(u)-6(b)7(u)-6(a)4(li)-3(ty)18( )-1046(re)4(d)-6( )-12u04(g)7(e)2(u)-6(l)i/euality redp9nS46(re)4(

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 ñscienceò mode. We took daily air samples for analysis for CH_4 levels and $^{13}/CH_4$ 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.

Many of the young people in the ñAtmospheric Groupò 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
samp8(w)15(a(t)-4(c)42re)4beeo0r ao0re604(tg8( )-2-2(p)-)-216k p8(w)N
pp th6(t)11(6(d)-6)-69lu4(xJ T* [(im)16(p)-6(( )-J 0 --2(re)4(su)-3(l42)4(re)
20rg 0 Tc 4-

Top-to-bottom: 7HVWLQJ VRLOV DQG ZDWHUV GHVFHQGLQJ RII WKH JODFLHU ZLWK SOHQW\ RI DLU VDPSOHV

Details of the equipment purchased for remote field work

1. Water quality testing kit: http://www.lamotte.com/environmental_education_monitoring.html

UK contact: www.sword-scientific.co

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

British Exploring

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

Andino, J. M., Wallington, T.J., Hurley, M.D., Wayne, R.P. A classroom demonstration of the formation of aerosols from biogenic hydrocarbons, J. Chem. Educ., 2000, 77, 1584-1586

Rockwell, D.M., Hansen, T. Sampling and analyzing air pollution, J. Chem. Educ., 1994, 71, 318-322.

Figure 1: 6XOIXU ZDVWH KHDSV LQ DW WKH 1HZWRQ ZRUNV RI -DPHV 0XVSUDWW DEDQGRQHG LQ 3KRWR

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 fromgalligu. 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.[9] Gossageôs 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 s ‹ / jA¤iðgä v ñ6) ä? ¤ 6g)`JL€b–ÄÑ‰°ñ1v ‘bƒ Öhh" ¨ílcfÖŠŽùÖ nF†

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 óthough 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 costô.[14] 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 U H J X O D W H G T X D Q W L W \ 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.[15]

Introduction

The legislative and fiscal dynamics of the waste manage-

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_{2eq} greenhouse gas emission savings when combined with the petrochemicals removed from the chemical supply chain.

Because Solvertôs process targets a feedstock that is geo-

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 (OH, HO_2 and RO_2) in the London environment. Radicals initiate and propagate the oxidation cycles that remove harmful trace gases (e.g. CO, benzene) from the atmosphere.

Leeds University's ground-based FAGE instrument[1,2], which uses laser-induced fluorescence (LIF) spectroscopy, has been deployed during the ClearfLo campaigns in London to quantify ambient hydroxyl (OH) and hydroperoxy (HO_2) radical concentrations. The instrument's measurement capabilities have also recently been extended to measure organic peroxy radicals (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.

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

Figure 1: %RWWRP WKUHH SDQHOV 7LPH VHULHV RI 52 +2 DQG 2+ UDGLFDO FRQFHQWUDWLRQV LQ XQLWV RI PROH FXOHV FP PHDVXUHG E\ WKH)$*(LQVWUXPHQW 0

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 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°N, 24.871°W) in the equatorial Atlantic Ocean, capable of separately measuring NO, NO_2, the sum of all peroxyacyl nitrates, the sum of all alkyl nitrates, HNO_3

Figure 3: 7LPH VHULHV RI 1O2 DQG 1O2 FRQFHQ WUDWLRQV UHFRUGHG RQ D ZLQWHU IOLJKW RYHU WKH 1RUWK 6HD VWDUWLQJ PLQXWHV DIWHU VXQVHW +LJKOLJKWHG LQ UHG DUH VHYHUDO WUDQVHFWV DFURVV WKH VDPH SROOXWLRQ SOXPH RULJLQDWLQJ IURP WKH /LYHUSRRO DQG 0DQFKHVWHU XUEDQ DUHDV (DFK WUDQVHFW LV PpÀHVS@ R£B 00W pPH WUI À°p V2WDRUSHQ Â˜óQeV‚Ð P

Figure 4: 7LPH VHULHV RI JO\R[DO PHWK\OJO\R[DO DQG 12 PHDVXUHG VLPXOWDQHRXVO\ E\ %%&($6 LQ D FKDP EHU VWXG\ LQWR WKH SKRWR FKHPLFDO R[LGDWLRQ RI DFHW\ OHQH 7KH DGGLWLRQ RI QLWURXV DFLG +212 DFWV ERWK DV D VRXUFH RI 12 12 DQG 12 DQG DV WKH SKRWRO\WLF VRXUFH RI 2+ UDGLFDOV ZKHQ WKH FKDPEHU URRI LV RSHQHG DW LQ RUGHU WR H[SRVH WKH JDV PL[WXUH WR OLJKW

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.
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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[1], Robert S. Blake[1], Iain R. White[1], Paul S. Monks[1], Fraser Reich[2], Steve Mullock[2] and Andrew M. Ellis
[1]Department of Chemistry, University of Leicester
[2]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.[1] 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 (VOC+H)$^+$ 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: $ SKRWRJUDSK RI WKH 375 7R) 06 LQVWUXPHQW ZLWK WKH GRXEOLQJ DV DQ LRQ IXQQHO OHIW ³%HI PDWLFV RI WKH LRQ IXQQHO ULJKW WKH GLRUHTXHQF\ HOHFWULF ILHOG LQVLGH W KRZ WKH 5) ILHOG JXLGHV LRQV WKURXJK \ PDVV VSHFWURPHWHU

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

The ability of low-cost, portable devices that incorporate electrochemical sensors to measure gases such as CO, NO and 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.[1]

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 was 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_2, CO, CO_2, SO_2, O_3, volatile organic compounds, size-speciated particulate matter and meteorological variables obtained using a high-density network of air quality sensors deployed in and around London Heathrow airport.

Figure 6: 6HOHFWHG &2 PHDVXUHPHQWV IURP WZR VHQ VRU QRGHV LQ SDUWV RI FHQWUDO &DPEULGJH VXSHUSRVHG RQ D URDG PDS 'DWD IURP SHULRGV ZKHQ WKH YROXQWHHUV FDUU\LQJ WKH VHQVRUV ZHUH ZDONLQJ WRJHWKHU DUH VKRZQ LQ UHG DQG JUHHQ DQG WKRVH IURP ZKHQ WKH\ ZDONHG DSDUW DUH VKRZQ LQ \HOORZ DQG EOXH

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

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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_3 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 (ñOPR methodò) provides a new way to monitor in situ chemical ozone formation, complementing traditional modelling approaches.[1] The principle of the OPR

Figure 7: $ FRPSDULVRQ RI VL]H GLVWULEXWLRQV IRU SXUH XQSURFHVVHG ROHLF DFLG DHURVRO SDUWLFOHV EOXH DQG WKHLU HTXLYDOHQW DIWHU H[SRVXUH WR SSP RI R]RQH UHG 'DVKHG OLQHV LQGLFDWH WKH PHDVXUHPHQW XQFHUWDLQW\ SUHFLVLRQ

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12. Bioaccessibility of the Inhalable Fra(S)-9-3(e)tio4(c)u U9L R³ly (R36(1((d)11((Du6( )-tID 6 >>BDC 0 0 1 rLang (nl-BE)d [(1)

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14. Characterization of Personal Exposures to and Indoor Concentrations of VOCs, $PM_{2.5}$, PAHs, Quinones and Black Carbon

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There is growing public awareness regarding the risks associated with poor indoor air quality in the home and workplace.[1,2] 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 request H G 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 $PM_{2.5}$ (particulate matter with diameters Ò 2.5 m) were found in the workplace, with an arithmetic mean of 30 ± 15 µg/m^3. These values are generally higher than the standard proposed by the World Health Organization (25 µg/m^3).[3] 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 ± 3,121 ng/m^3), whilst the highest concentrations measured indoors were in pubs and restaurants (2,901 ± 4,229 ng/m^3).

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

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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.[1,2]

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

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(a)4(n)-6(is)a8(n)18(s)-1Stiveaptom6tentiaMaft(a)4onaiM-vChensiM3(o)s4-2F(M)

Rof S(c)-3ib(t)-10tyof-Ch(e)4(m -23ib-5(s)-5str)-15(y)]TJ/C2_3 92.96 f 12 0.206 0 Td<00B2>Env63ib-5trm -23eonal

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

Forthcoming symposium

The history of the chemical industry in the Runcorn Widnes area

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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 & % (' 6 F 5 X Q F R U Q ¶ V & K H P L F D O) R X Q G D W L R Q R U / R F D W L R Q

11.30