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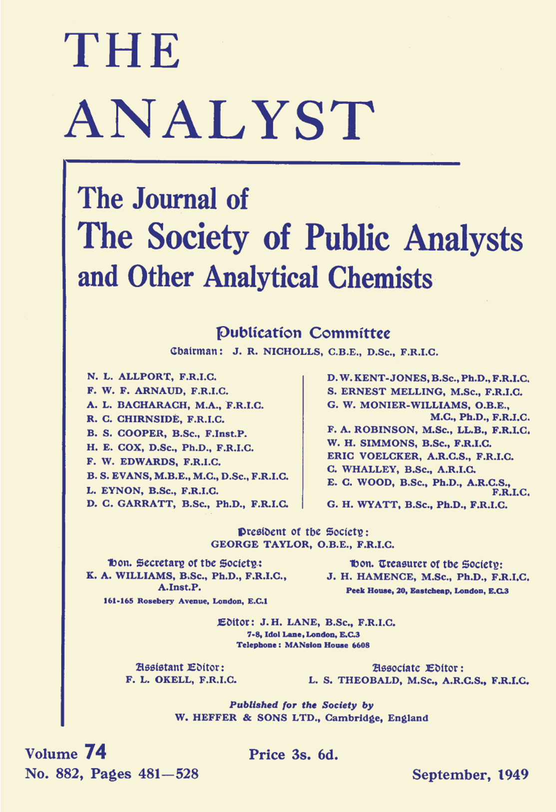
Bulletin



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and Other Analytical Chemists

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In this issue

The September 1949 edition of *The Analyst* contained the world's first report of the contamination of groundwater by a chlorinated solvent. On pp 5-14 of this issue, **Michael Rivett** explains why this pioneering work by two British Public Analysts, Frances Lyne and Thomas McLachlan, lay dormant in the scientific literature for so long.

Also

Other examples of the pollution of water (and soil and atmospheric) environments are described. **Roger Reeve** reviews recent advances in the biodegradation of pharmaceutical products in sewage works. **Vernon Somerset** reports on the first mercury reference laboratory to be established in Southern Africa. **Victoria Holmes** summarises progress on the rehabilitation of Loe Pool, Cornwall. And **James Lymer** explains his work on the assessment of contaminated land and the recently published CL:AIRE report, *The Soil Generic Assessment Criteria for Human Health Risk Assessment*.

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ECG *Bulletin*

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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.

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This and previous issues of the *Bulletin* are available without charge online at www.rsc.org/ecg. Each member of the Environmental Chemistry Group also receives two issues per year of the printed ECG *Bulletin*. For membership details visit www.rsc.org/Membership.

Chairman's report 2009

During 2009 the Environmental Chemistry Group Committee has continued with its regular activities: production of the ECG *Bulletin*, maintenance of the ECG web pages (www.rsc.org/ecg), and organisation of the Distinguished Guest Lecture (DGL) and other symposia.

DGLs present and future: The ECG's annual DGL and Symposium has a long-standing tradition of attracting eminent and engaging speakers, including Nobel Prize winners, from across a spectrum of fields, which both inform and expand our understanding of the environment through chemistry. The topic for the 2009 Distinguished Guest Lecture and Symposium (the 36th), held on March 4th, was *The Future of Water* and, although centred on a very interesting and topical subject, it failed to draw the audience numbers expected, due in part, it was suggested, to insufficient publicity. The ECG Committee debated as to whether future DGLs should return to more chemistry-focused topics but it was also argued that the broader remit offered a more interesting range of presentations with wider appeal, as shown by the larger audiences of the recent years' DGLs and Symposia.

The 2009 DGL speakers were Dr John W. Sawkins (Heriot-Watt University); Professor Richard C. Carter (Cranfield University); Lars Steffensen (Ebullio Capital Management LLP); Dr P. B. Anand (University of Bradford); Professor Tony Allan, (King's College London) (Distinguished Guest Lecturer). A summary of this meeting appeared in the July 2009 issue of the ECG *Bulletin*.

The 2010 DGL and Symposium has the title *King Coal: future prospects for growth, use and clean technologies*, and the Distinguished Lecturer will be **Professor James Sumner Harrison**, Chairman of the British Coal Utilisation Association, who will talk on "Advances in the technology of the use of coal". This meeting will be held in the Library of the Royal Society of Chemistry (part of the new Chemistry Centre) on Wednesday 24th March 2010, and further details are on pp 28-30 of this issue.

Other 2009 ECG symposia: ECG committee members **William Bloss** and **Stephen Ball** organised the first ECG *Atmospheric Chemistry Student Forum* on April 2nd 2009 at Burlington House, London. This successful event was well-attended and all 25 delegates contributed either oral or poster presentations. A keynote address was given by Professor Mike Pilling on 'Uncertainties in atmospheric chemistry', and an expert panel of Adrian Kybett (York), Jacqui Hamilton (York) and Caroline Tolland (RSC Careers Advisor) dispensed careers advice in a 'Question Time'-style session. The delegates, predominantly PhD students, were attracted by the travel bursary and free admission on registering as RSC members, which has led to 12 RSC and ECG recruitments. A summary of this meeting appeared in the July 2009 issue of the ECG *Bulletin*, and a selection of abstracts is presented in this issue (pp 37-40).

In September 2009, ECG committee member **James Lymer** organised a meeting on contaminated land: *Contaminated Land: Contaminant Transport and Fate* again at Burlington House. This one-day meeting was aimed at scientists and policy makers involved in the assessment and remediation of contaminated land. More than thirty delegates from a wide range of organisations, including consultancies, regulators and academia, took part in a detailed discussion on contaminant transport and fate in soil and groundwater. Presentations were given by Professor Andrew Hursthouse (West of Scotland) 'Contaminated land regulation: science policy issues and pollutant dynamics'; Professor Steven Banwart (Sheffield), 'Novel laboratory methods to study reactive transport of organic pollutants in groundwater'; Dr Chris Collins (Reading), 'Importance of chemical properties in estimating exposure to chemicals'; Dr Mike Rivett (Birmingham), 'The legacy of chlorinated solvents in contaminated land and groundwater'; and Dr David Werner (Newcastle), 'Persistent organic contaminant availability in sediment: Improved risk assessment and novel remediation approaches'. The day's proceedings concluded with a question-and-answer session chaired by Andrew Hursthouse. This event was funded by delegates' fees, a grant from ESEF and was co-sponsored by Wardell Armstrong.

For 2010, the ECG's planned events include a joint ECG/Toxicological Group meeting on contaminated land in September, a second ECG *Atmospheric Chemistry Student Forum* provisionally booked for late 2010 (or possibly for the first part of 2011), and a conference on metal speciation to take place in September 2010.

ECG committee: Six new ECG committee members were elected at the 2009 ECG AGM, four were retained (Bill Bloss, Stephen Ball, James Lymer, Roger Reeve (now an attending member)), two left the committee (Adrian Kybett, Andrew Parker), and one new member has been co-opted (Imad Ahmed from the University of Lancaster). Brendan Keely (the current Vice-Chair) will leave the committee after the 2010 AGM in March. The number of ECG committee meetings held each year has been reduced and meeting times changed to minimise travel costs.

DGLs past: In June 2000, in my Chairman's Report on the DGL Symposium of that year (*Climate Change and its Impact*) (*ECG Newsletter* Issue No. 12), I commented:

"It is beginning to become apparent that the global commitment to ameliorating the rate of climate change is decidedly weak. Whether this is because the effects of change on the Western Hemisphere are predicted to be tolerable, or whether it is because the actions needed are too difficult to implement, it appears that the political will, the economic imperatives, and the concerns for the world's ecosystems are not strong drivers for behavioural change."

Ten years on the question is whether things have changed? Have we now reached a seminal point in the history of man where coherent international action of the necessary intensity can be agreed?

During his 2000 Distinguished Guest Lecture, Sir John Houghton mentioned pioneering studies in atmospheric chemistry carried out by the physical chemist and Nobel Prize winner Svante Arrhenius. Following on from this reference, I quote from Patrick Coffey (*Cathedrals of Science: The Personalities and Rivalries that Made Modern Chemistry*, Oxford University Press, Oxford, 2008, p. 27 (ISBN 978-0195321340)):

"With his return to Sweden, Arrhenius essentially abandoned physical chemistry, although he welcomed to his laboratory visiting scientists and students in the field. He took up instead what he called "cosmic physics," which would be called earth sciences today. Beginning in 1894, he was the first to construct a quantitative model of the greenhouse effect, linking variations in the carbon dioxide content of the atmosphere to climate change. He performed elaborate calculations recording measurements every ten degrees of latitude at different seasons, used the observed reflectivity of the moon as a reference for the sun's radiative energy, and developed a model of the relationship between carbon dioxide and surface temperature: the changes in temperature would vary as the square of the carbon dioxide concentration. And the effect would be greater in the summer than in winter. He predicted that doubling the carbon dioxide concentration would increase the mean temperature 6 °C … ."

The question I ask is: what sort of a society is it when a large number of people cannot understand the simple truth of this 100-year old argument?

Svante Arrhenius

Arrhenius's prescience about the link between changes in atmospheric CO_2 concentrations and climate is reinforced by data on greenhouse gases and on the world's climate, which the World Meteorological Office (WMO) published in November and December 2009. In 2008, global concentrations of carbon dioxide, methane and nitrous oxide reached the highest levels recorded since pre-industrial times. Since 1990, the overall increase in radiative forcing caused by all long-lived greenhouse gases is 26% and the increase was 1.3% from 2007 to 2008. For carbon dioxide in particular, global concentrations reached 385.2 ppm in 2008 – an increase of 2.1 ppm from the previous year, continuing the tendency of exponential increase. The year 2009 is likely to rank in the top 10 warmest on record since the beginning of instrumental climate records in 1850. The global combined sea-surface and land surface air temperature for 2009 (January–October) is currently estimated at 0.44° C ± 0.11°C (0.79°F ± 0.20°F) above the 1961–1990 annual average of 14.00° C/57.2°F. The current nominal ranking of 2009, which does not account for uncertainties in the annual averages, places it as the fifth-warmest year. The decade from 2000 to 2009 was warmer than the decade from 1990 to 1999, which in turn was warmer than from 1980 to 1989. More complete data for the remainder of 2009 will be analyzed at the beginning of 2010 to update the current assessment.

FOOTNOTE: A pdf version of Svante Arrhenius's paper "On the Influence of Carbonic Acid in the Air upon the Temperature of the Ground", *Philos. Mag.*, Series 5, Volume 41, April 1896, pages 237-276 accompanies the web version of this issue of the ECG *Bulletin*.

An 'Historical Overview of Climate Change Science' was published in the 2007 IPCC Report: *Climate Change 2007: The Physical Science Basis*, Contribution of Working Group I to the Fourth Assessment Report of the IPCC (ISBN 978 0521 88009-1 Hardback; 978 0521 70596-7 Paperback) at:

http://www.ipcc.ch/pdf/assessment-report/ar4/wg1/ar4-wg1-chapter1.pdf

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December 2009

The legacy of chlorinated solvents in groundwater: an overlooked 1940s contribution

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Dr Michael Rivett from the University of Birmingham recounts some pioneering work in environmental chemistry carried out by two Reading-based analytical chemists – Frances Lyne and Thomas McLachlan.

Introduction

Industrial chlorinated solvents have become widespread pollutants of groundwater. General awareness of the solvents-in-groundwater problem emerged in the 1970-80s, some 50 years after the onset of their industrial use. By this time large amounts of solvent had been used, and disposed of, with poor environmental awareness. The legacy of subsurface solvent pollution may be substantial, persistent, subject to legal action, and very costly to remediate. Interestingly, two members of the Royal Society of Chemistry, Frances Lyne and Thomas McLachlan, published a short paper in 1949 about solvent pollution of groundwater wells. Unfortunately, it appears their work has been largely overlooked by the scientific community.

The solvents-in-groundwater problem

The apportionment of legal liability in cases of land and groundwater pollution may depend upon an alleged polluter's awareness of an incident, and whether they could have reasonably foreseen the adverse consequences of their actions. In assessing foreseeability, one consideration is the published information at the time of pollutant release to determine whether there was a general recognition that the activities may have reasonably been foreseen to cause contamination problems. Historic cases of groundwater contamination are hence important in this regard. A short paper by Lyne and McLachlan (1949) has recently resurfaced from the literature describing historic cases of the now notorious groundwater pollutant trichloroethene (TCE, trichloroethylene, $Cl_2C{=}CHCl$). This paper is believed to be the earliest journal publication worldwide on this class of environmental pollutant. It is hence important, and has been the subject of recent publications and debate (Colten & Skinner, 1994, 1996; Rivett *et al.*, 2006; Rivett & Clark, 2007; Amter & Ross, 2008; Rivett 2008). A review of that interest, based largely on Rivett *et al.* (2006) and Rivett (2008), is presented in this article.

By the mid to late 1980s, it was clear internationally that chlorinated solvents, for example trichloroethene, 1,1,1-trichloroethane (TCA, Cl_3CCH_3), and tetrachloroethene (perchloroethylene, PCE, $Cl_2C{=}CCl_2$), were very prevalent groundwater contaminants (Mackay and Cherry, 1989; Schaumburg, 1990; Rivett *et al.*, 1990). Chlorinated solvents, typically C1-C2 chlorinated aliphatic hydrocarbon (CAH) alkenes/alkanes, have been used widely by industry since the 1920-30s (Rivett *et al.*, 1990), often as a general purpose degreaser. TCE was extensively used in metal fabrication and engineering, PCE in textile and leather degreasing and TCA in circuit-board manufacturing (Pankow *et al.*, 1996). ICI (Imperial Chemical Industries plc) has been the UK's principal manufacturer at its Runcorn plant. Limited quantities of TCE were produced until 1927 when suitable degreasing containers were developed, resulting in UK productivity expanding to *ca.* 40,000 tons p.a. by 1949 and peaking at *ca.* 90,000 tons in 1970 (Rivett *et al.*, 1990). Shortly after this peak, the chronic carcinogenicity of TCE was recognised in 1975 (NIOSH, 1975). This led to low µg/L drinking-water standards being established, reduced TCE/PCE production, and some replacement by TCA until the latter's atmospheric pollution potential was recognised. Acute health effects from occupational exposure to TCE have been known since the 1930s (Stuber, 1932).

Chlorinated solvents are a challenging groundwater problem for a variety of reasons. They are dense non-aqueous phase liquids (DNAPLs) that are immiscible with water, but still sufficiently soluble to exceed drinking-water standards by several orders of magnitude. Their denser-than-water nature combined with their low viscosity may permit very rapid penetration of DNAPL solvents far below the water table in many aquifers (Mackay and Cherry, 1989). Often the recommended practice for disposal of used solvents, up until the 1970s and perhaps beyond, was to pour solvents onto the ground (or pits) to allow solvents to evaporate – with or without ignition; there was significant potential for rapid infiltration of solvent DNAPL into the subsurface. Such disposal practices and inadvertent spillages have led to many DNAPL sources being present in aquifers, often at depths where other pollutants may never reach. Such DNAPL may typically persist for decades (Rivett & Feenstra, 2005) and slowly dissolve to yield persistent groundwater plumes that can extend up to kilometre scales and more (Jackson 1998). There have been many high-profile sites, some with contentious legal cases that can involve tens and in some cases millions of dollars of site investigation and remediation works (Misstear, 1998; Kirtland *et al.*, 2003; Oostrom *et al.*, 2007).

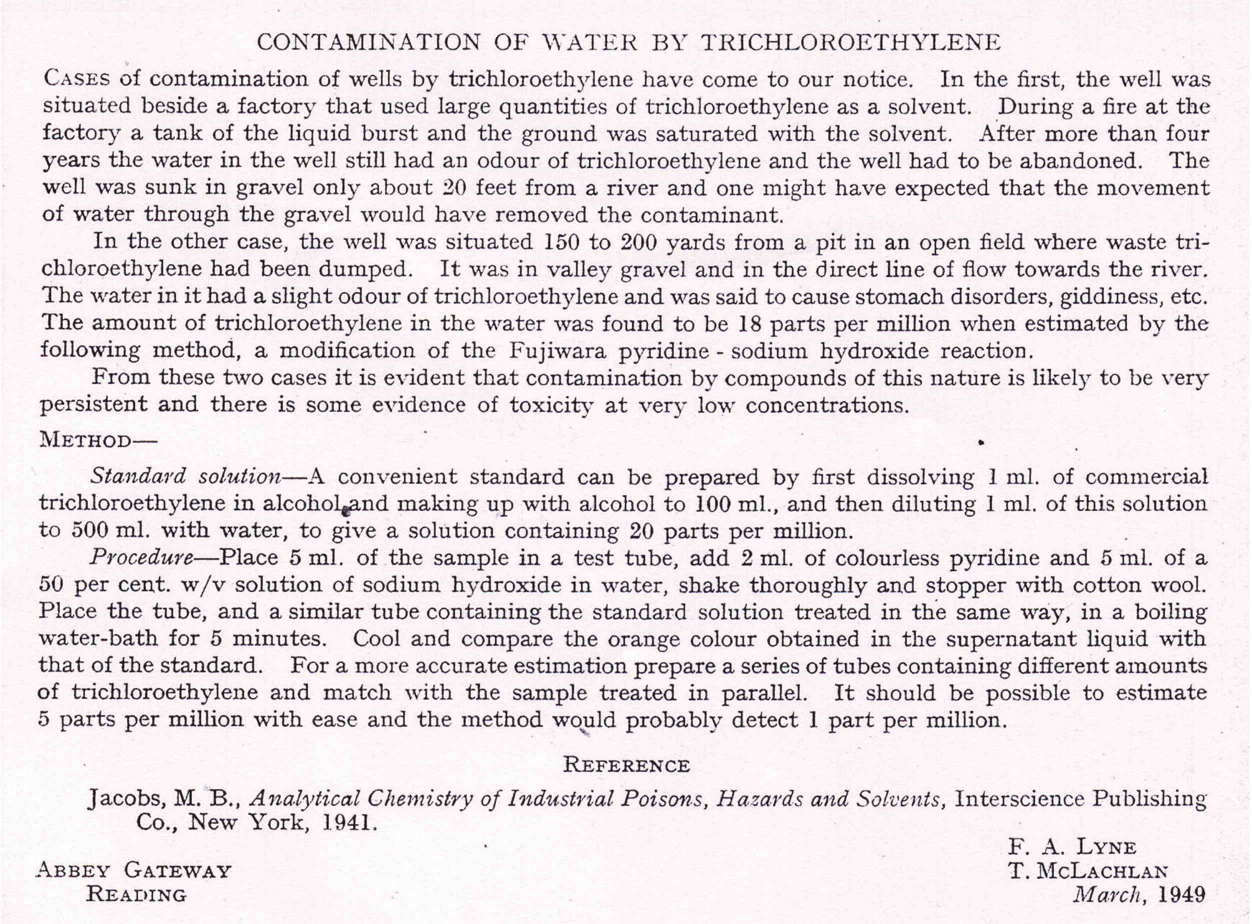
Lyne & McLachlan (1949)

Some 60 years ago, two UK chemists, Lyne and McLachlan, published "*Contamination of water by trichloroethylene*" (Lyne & McLachlan, 1949). Their entire paper is reproduced in **Figure 1** and was originally published in the journal *The Analyst*. Despite its brevity, the paper has significant content. Two separate cases of groundwater wells contaminated by TCE are described, arising from a tank release and a suspected leaking disposal-pit. Human-health effects are reported, e.g. stomach disorders, giddiness. A colorimetric method of analysis was described to quantify TCE concentrations in water. A concentration of 18 mg/L TCE in groundwater from a supply well was recorded (the first measurement worldwide) that exceeds current drinking water standards by a thousand-fold. A perceptive conclusion was reached: "*that contamination by compounds of this nature is likely to be very persistent*"; a conclusion that is all too evident nowadays. As noted by Travis (1998), their conclusions were certainly worthy of more than passing notice, particularly since they drew attention to the threat to human health. Also, as explored by Rivett *et al.* (2006), in terms of wider liability and foreseeability, a fundamental question is – did Lyne and McLachlan (1949) trigger any recognition of the problem of groundwater contamination by TCE, or similar chlorinated solvents, at either a local, national or international level?

Frances A. Lyne and Thomas McLachlan

Little information is given in the publication (**Figure 1**) concerning the authors, whose affiliations were disclosed as "*Abbey Gateway, Reading*". Lyne and McLachlan were both members of the Royal Society of Chemistry (RSC) (and some of the constituent societies of the RSC before the amalgamation in 1980*). The RSC confirms that Mr Frances Arthur Lyne was born in 1913, died in 1996 and was a member of the RSC from 1934 until his death aged 83 years. Mr Thomas McLachlan was born in 1894, died in 1991 and was a member of the RSC from 1917 until his death aged 97 years. Although Lyne and McLachlan both lived into the 1990s and hence beyond the general 1970-80s period of recognition of the solvents-in-groundwater problem, there unfortunately appears to have been no detailed consultation with them concerning their 1949 paper before their deaths.

'The County Borough' section of the 1941 Nov. issue of *The Reading Mercury* indicates "*Mr Thomas McLachlan FIC of ... London ... has been appointed .... as public and agricultural analyst for the County of Berkshire. He is to open a laboratory in Reading, and it is understood that he will act in a similar capacity for the Borough*". Analysts were officially appointed and authorised to provide certified (chemical) analyses. The Kelly's Directory of Reading 1949 indicates: "*Public Analysts: Thomas McLachlan ACGFC FRIC (& Official Agricultural Chemist) & Frances Arthur Lyne FRIC, Abbey Gateway, Abbey St. Listed under 'Officers of the Corporation and Urban Sanitary Authority' so employed in that capacity by the Borough of Reading.*" The same directory also lists Thomas McLachlan as "*County Analyst (Food & Drugs & Fertilisers & Feeding Stuffs Acts)*" at the same address. Part of an obituary by Lyne (1992) on McLachlan published in *Chemistry in Britain* confirms the above and more: "*During World War II McLachlan's laboratory in central London was badly damaged but he moved to various locations including the Pharmaceutical Society in Bloomsbury Square. He showed great fortitude and tenacity in carrying on his professional work in spite of adversity resulting from enemy action. In 1942 McLachlan was appointed public analyst for Berkshire and the City of Oxford, and in partnership with F.A. Lyne opened a laboratory in Reading, in addition to his London laboratory.*" Travis (1998) further summarises Lyne and McLachlan's public analyst appointments. He notes that in the late 1930s Lyne was the Public Analyst for Chelsea and authored 1941-42 public analyst reports for Fulham. In 1949 both Lyne and McLachlan gained Public Analyst responsibilities for Windsor (Berkshire) and Oxford, and McLachlan was also appointed Public Analyst for Thurrock, Essex. McLachlan was a founder member of the Association of Public Analysts.



CONTAMINATION OF WATER BY TRICHLOROETHYLENE

Cases of contamination of wells by trichloroethylene have come to our notice. In the first, the well was situated beside a factory that used large quantities of trichloroethylene as a solvent. During a fire at the factory a tank of the liquid burst and the ground was saturated with the solvent. After more than four years the water in the well still had an odour of trichloroethylene and the well had to be abandoned. The well was sunk in gravel only about 20 feet from a river and one might have expected that the movement of water through the gravel would have removed the contaminant.

In the other case, the well was situated 150 to 200 yards from a pit in an open field where waste trichloroethylene had been dumped. It was in valley gravel and in the direct line of flow towards the river. The water in it had a slight odour of trichloroethylene and was said to cause stomach disorders, giddiness, etc. The amount of trichloroethylene in the water was found to be 18 parts per million when estimated by the following method, a modification of the Fujiwara pyridine - sodium hydroxide reaction.

From these two cases it is evident that contamination by compounds of this nature is likely to be very persistent and there is some evidence of toxicity at very low concentrations.

Method—

Standard solution—A convenient standard can be prepared by first dissolving 1 ml. of commercial trichloroethylene in alcohol and making up with alcohol to 100 ml., and then diluting 1 ml. of this solution to 500 ml. with water, to give a solution containing 20 parts per million.

Procedure—Place 5 ml. of the sample in a test tube, add 2 ml. of colourless pyridine and 5 ml. of a 50 per cent. w/v solution of sodium hydroxide in water, shake thoroughly and stopper with cotton wool. Place the tube, and a similar tube containing the standard solution treated in the same way, in a boiling water-bath for 5 minutes. Cool and compare the orange colour obtained in the supernatant liquid with that of the standard. For a more accurate estimation prepare a series of tubes containing different amounts of trichloroethylene and match with the sample treated in parallel. It should be possible to estimate 5 parts per million with ease and the method would probably detect 1 part per million.

Reference

Jacobs, M. B., *Analytical Chemistry of Industrial Poisons, Hazards and Solvents*, Interscience Publishing Co., New York, 1941.

F. A. Lyne
T. McLachlan
March, 1949

Abbey Gateway
Reading

Figure 1. *Manuscript of Lyne and McLachlan (1949).* The Analyst, *1949,* ***74****(882), 513, DOI: 10.1039/AN9497400510 – Reproduced by permission of the Royal Society of Chemistry. This article is available as part of the Royal Society of Chemistry Journals Archive at www.rsc.org/archive.*

The Reading address was primarily connected with their Public Analyst responsibilities for the Borough of Reading and for the wider County of Berkshire of which Reading is the County Town. In relation to the Reading/Berkshire positions, McLachlan was appointed around late 1941 and was still County Analyst in 1964 (aged 70). Lyne was still in his post as Public Analyst at least until 1975 (aged 62). Their 1940s laboratory was in Abbey Gateway, Abbey Street, Reading. This was located near the main entrance to the old Abbey near the centre of Reading (**Figure 2**). It is probable they had a floor of the present Crown Court, then predominantly the Berkshire County Police Headquarters. Lyne remained professionally involved into his 70s. Lyne headed the *Lyne, Martin & Radford Public Analyst* – a commercial laboratory based in Reading. Martin was a Public Analyst colleague of Lyne's for several decades and was later joined by Radford.

Figure 2. *The Abbey Gateway in Reading, Berkshire (2004) where Lyne and McLachlan's laboratory was located in 1949 [from the address given in Lyne & McLachlan (1949)]*

The case study sites

Significant effort was made by Rivett & Clark (2007) to locate the unidentified case-study sites described by Lyne & McLachlan through archive records, consultations with relevant professionals and field reconnaissance of the Reading area. Some potential sites were identified. However, none could be confirmed. This is ascribed to the brief descriptions given in the paper, the lack of relevant historic record keeping and the relatively wide pre-1949 jurisdictional area covered by Lyne and McLachlan. It is more probable, although not proven, that the sites were located in the Reading area based upon:

- the Reading address where they worked in 1949;
- the industrialized urban nature of this location;
- the area contained a significant density of small-medium engineering works with war-time aircraft manufacture prominent (e.g. at least four aircraft-related sites in central Reading with the Miles Aircraft main factory on the outskirts at the Woodley aerodrome site);
- the hydrogeology of the region – the Thames Valley gravel aquifer along with three main rivers.

However, failure to locate these sites today does not detract from the significance of Lyne and McLachlan's paper.

Influences of Lyne and McLachlan (1949)

The relevance and influence of any published paper is subjective with different views possible. This is the case for Lyne and McLachlan (1949) as set out in the discussion (Amter & Ross, 2008) and reply (Rivett, 2008) to Rivett *et al.* (2006). The influence of Lyne and McLachlan (1949) may be considered under various headings: literature citations of Lyne and McLachlan (1949) from the scientific, technical and legal case literature and records; Lyne and McLachlan's later careers and publications; local, national and international recognition of the 'solvents-in-groundwater' problem; and use of the analytical method described in their paper.

Literature citations to 'Lyne and McLachlan'

General recognition of the solvents-in-groundwater problem began from the mid-to-late 1970s to 1980s (Pankow *et al.*, 1996). This was some twenty-five years or more after Lyne and McLachlan's 1949 publication and suggests that the influence of their work was limited. Citations of Lyne and McLachlan prior to *ca.*1980 are the most relevant to assessing the paper's influence on problem recognition. It is always difficult to assure complete coverage of citing works, particularly of the grey literature, and indeed Amter & Ross (2008) add to those citations indicated by Rivett *et al.* (2006) with further response to those provided by Rivett (2008).

Lyne & McLachlan (1949) were cited four times between 1950 and 1951: *Chemical Abstracts* (1950); *Water Pollution Abstracts* (1951); Rudolphs, W. (1951) (*Sewage and Industrial Wastes*); and Love, S.K. (1951) (in a review of water analysis methods). Thus Lyne and McLachlan's 1949 paper was widely noted in abstract or review literature by the scientific community in 1950-51, but mainly for its analytical method. The paper was then mentioned by Jettmar (1957) in an informative review of groundwater contamination which appeared in a German-language Austrian journal. Jettmar (1957) (but not Lyne and McLachlan) was cited again in an annotated bibliography on groundwater pollution (Summers & Spiegel, 1974). The only other significant citation to Lyne and McLachlan (1949), which partly recognised the importance of the groundwater context, was by Stanley and Eliassen (1961) in their "*Status of Knowledge of Groundwater Contaminants*" produced for the US Federal Housing Administration (FHA). A brief factual paragraph is found at the end of the section on "Pesticides – Experience to date"; inclusion within that section detracts from the recognition of TCE's significance.

Lyne & McLachlan (1949) are additionally cited in:

- Klein (1957) (and 1962 update), a book on pollution of rivers, which reports Lyne and McLachlan's analytical method;
- Schollmeyer (1960), a German-language paper which applies Lyne and McLachlan's analytical method to biological samples;
- Mancy & Weber (1971), who cite Lyne and McLachlan's colorimetric analytical method for the analysis of chemical wastewater;
- NAS (1975), where Lyne and McLachlan (1949) are cited as an example of how production-plant losses of chlorinated hydrocarbons to the environment may cause contamination of water wells. (In fact the cases quoted were solvent-user industries, rather than production plants).

There are two other indirect citations of Lyne and McLachlan's work *via* Jettmar (1957), within the pesticide-based literature of USPHS (1964) and Cope (1966). These references are distorted and muddled third-hand accounts that categorise the work within the emerging pesticide literature and serve little to exemplify the influence of Lyne & McLachlan's work, in fact rather the opposite.

Rivett (2008) concluded that none of the aforementioned documents, though citing the Lyne & McLachlan article, support a conclusion that Lyne & McLachlan triggered recognition of the problem of groundwater contamination by TCE or other solvents at a local, national or international level during the 1950s through to the 1970s. Certainly the citations indicate an awareness of Lyne & McLachlan's work, however, this interest is largely peripheral with citing authors mostly concerned with the analysis method for other water/sample types, pesticide contamination and ocean pollution. There are only five citations (three direct, two indirect citing Jettmar) that present the groundwater pollution finding of Lyne & McLachlan at all. All are very factual, none develop significantly the implication of the article, and some are misrepresenting. Based on the published literature, the groundwater pollution aspect of Lyne & McLachlan's 1949 paper was therefore insignificantly recognised over the crucial 1950-75 period.

Subsequent work by Lyne and McLachlan

A brief review of Lyne and McLachlans' later careers failed to find evidence of subsequent work published by them on solvent-contaminated sites. Lyne continued to work with the Reading Borough Council within environmental health roles until his retirement. Although the remit of local authorities still included water-related health issues, much work may have likely focused on other topics such as air and food quality. Additionally, from around the 1950s groundwater management in the UK increasingly moved from local authority control to the regional water authorities or companies, and later the national regulator (Environment Agency, previously the National Rivers Authority). Lyne additionally headed the *Lyne, Martin & Radford* Public Analyst laboratory that analysed soil/water samples in the 1970–80s – according to reports from my own colleagues who were working at that time on solvent-contaminated sites. However, *Lyne, Martin and Radford's* remit was to analyse the samples provided to them, with no direct site involvement or interpretation of site data.

Other publications by Lyne and McLachlan reflect their predominant public analyst/environmental health-based analysis work, which was wide-ranging. McLachlan has at least forty and Lyne at least seven publications in the scientific literature. Their publications include (citations are not listed here, but may be found in Rivett *et al.*, 2006): "The analysis of starch sugar degradation products by selective fermentation" (McLachlan, 1928); "Drinking waters for cattle" (McLachlan, 1930); "The analysis of green teas" (McLachlan and Stern, 1934); "The treatment of waste waters in the food industry" (McLachlan, 1935); "Notes on the selective oxidation of vinegar" (Lyne and McLachlan, 1946); "Use of anthrone in the determination of trace amounts of glycerol" (Lyne *et al.*, 1968); and by McLachlan, "A new approach to the analysis of fish cakes" (Burgess *et al.*, 1970).

Publications in their later life are informative of their interests over that period when the solvents problem was generally emerging. These are foodstuff-related and include reviews of the starch analysis literature by Lyne (1976) and "Health foods – a Public Analyst's view" by McLachlan (1972). McLachlan's final publication (McLachlan, 1983) was published when he was 89 years old and is simply entitled "Old age"! Lyne's final publication was in fact a short obituary of McLachlan (Lyne, 1992). He makes no reference to their joint work on TCE, rather, he notes McLachlan's pioneering work on building decay relating to air pollution and microbiological action (McLachlan, 1940). No further publications by Lyne and McLachlan on TCE, chlorinated solvents, or groundwater have been found after their 1949 paper.

Recognition of the solvents-in-groundwater problem

Rivett *et al.* (2006) review in detail the recognition of the solvents-in-groundwater problem in the UK and internationally. There is no evidence that Lyne and McLachlan's work and their continued presence in Reading generated any early appreciation of the solvents-in-groundwater problem, either locally in the Reading area or in the UK. Review of UK groundwater-contamination literature has failed to uncover any UK authors citing Lyne and McLachlan (1949) until recently (Rivett *et al.*, 2005). It is doubtful that any of the UK groundwater or geosciences practitioners would have subscribed to *The Analyst*, and it would appear that the UK water-related research community remained oblivious to the paper's existence.

Some early references to potential TCE groundwater problems occurred in the late 1960s to early 1970s. For example, Section III, para. 32 of a toxic waste disposal report identified TCE as a threat to water quality (Ministry of Housing and Local Government, 1970). Waste Management Paper No. 9 (DoE, 1976), a guidance on the disposal of halogenated hydrocarbon solvents, also recognised the threat. Groundwater quality work in the 1960s-70s, however, focused on landfill, nitrate and sewage effluent pollution. Limited, proactive, investigation of chlorinated solvents in groundwater did occur under the DoE (Department of Environment) research programme into pollution from landfills (DoE, 1978), with analysis and detection of chlorinated solvents in the chalk unsaturated zone below the Ingham landfill site (Suffolk) in 1974. ICI appears to be the earliest industry to assess the impact of chlorinated solvents to the UK environment in the early-to-mid 1970s (Pearson and McConnell, 1975). ICI's monitoring programme over 1972-73 was largely in the vicinity of its main Runcorn production facility. Pearson and McConnell (1975) reported chlorinated solvents at parts per billion or less in freshwaters, sea waters and marine sediments. They did not directly report their groundwater data, but indicate "*Significantly we have never detected organochlorines in well waters*". This early work still failed to trigger solvent problem recognition. Yorkshire Water Authority workers Stanton and Firth (1978) tentatively identified PCE in some groundwater samples during trihalomethane (THM) surveys of water supplies. The often presumed earliest UK case of TCE/PCE detected in groundwater was in the limited groundwater supply surveys of Fielding *et al.* (1981). The first national groundwater survey (209 sites) was not conducted until 1984 and revealed significant TCE contamination (Folkard 1986).

The UK's most notable groundwater-contamination legal case involved PCE contamination of the Cambridge Water Company Sawston borehole in 1983 (Misstear *et al.*, 1998). Following discovery of the pollution in 1983 and subsequent investigations, the case was heard in the High Court in 1991, the Court of Appeal in 1992, and was finally decided by the House of Lords in 1993. Common Law principles applied. The Lords decided recovery of damages in nuisance depended on foreseeability, *and the alleged polluter could not have reasonably foreseen the consequences of the solvent release at that time*. The key question was the date at which a 'solvent user' was reasonably able to foresee the potential harm that solvents could cause in the aquatic environment. The Lords decided this was after 1976. This date was based upon concerns beginning to be expressed around that time on the presence in groundwater of low PCE and TCE concentrations as potential carcinogens, and the publicity this issue was receiving outside of scientific journals (NIOSH, 1975). The case appears to have been completely unaware of the existence of Lyne & McLachlan (1949).

Internationally, after Lyne and McLachlan's early work, it appears that Schwille, the pioneer of DNAPL solvents research (Schwille, 1988), should be credited with the earliest proactive investigation of groundwater contamination by solvents. Schwille in the late 1990s prepared an unpublished report describing the reasons for his early recognition of the solvents problem (personal communication, Cherry, J.A.). He details two TCE case studies in Germany, in 1967 and 1973, that were not made public. There is no mention of Lyne and McLachlan in Schwille's reporting. Furthermore, none of the other European publications that reported early discoveries of solvent contamination of groundwater make any reference to Lyne & Mclachlan. These include Grob and Grob (1974) and Giger and Molnar-Kubica (1978) in Switzerland, who accidentally discovered PCE contamination of wells while testing the tap water in their own laboratory. Also included in this early work is (probably) the first European national survey, in The Netherlands, where analysis for halogenated VOCs (volatile organic compounds) was conducted in all of the nation's 232 ground-water supplies during 1976-78 (Zoeteman *et al.*, 1981). Trichloroethylene was the predominant VOC detected.

Recognition of the solvents problem in the US has been reviewed by Pankow *et al.*, 1996; Jackson 2004, 2003; and Amter & Ross, 2001. Stanley and Eliassen (1961) cited Lyne and McLachlan, but this did not stimulate any general recognition of the contamination problem. Not until the mid-to-late 1970s was the problem properly recognised in the US. It has been argued that recognition of the solvents problem should have been foreseen much earlier, in the 1940-50s (the era of Lyne & McLachlan) (Amter and Ross, 2001; Travis, 1998). However, there are almost no publications before 1975 that confirm solvent concentrations in US groundwater. Exceptions to this are reports in a 1961 US Public Health Service symposium (Middleton &Walton 1961; Miller 1961). The former paper listed TCE as an organic chemical that had caused one or more cases of groundwater contamination in the US; the sites in question, though, have not been determined. Occasional early references (Banks and Lawrence, 1953) make general remarks to the potential for solvents to cause groundwater problems, but it cannot be determined whether such remarks referred to chlorinated solvents *per se*, or to other miscible solvents or petroleum distillates discussed elsewhere in the 1950-60s literature.

The discovery by Rook (1974) in The Netherlands of trihalomethanes (THMs) formed during the chlorination of water containing humic compounds (and more routine availability of improved gas chromatography (GC)) was pivotal. This led to widespread testing for THM and other chlorinated solvents in US public water supplies, including some from groundwater. US EPA national surveys in 1974-76 (Symons *et al.*, 1975; Brass *et al.*, 1977) revealed the presence of chlorinated compounds and led to the conclusion between *ca.*1976-79 that many groundwaters were contaminated with chlorinated solvents (Pankow *et al.*, 1996). Thus the widespread discovery of chlorinated solvents in groundwater was somewhat fortuitous and essentially derived from increased public health concerns over THMs. Concurrently, TCE and PCE were identified as potential carcinogens (NIOSH, 1975, 1978). Hundreds of solvent-contaminated sites were documented by 1980 in the US. Emergence of the solvent problem there thus preceded events in the UK, but likewise appears uninfluenced by Lyne & McLachlan's early work.

Lyne and McLachlan's analytical method

Lyne and McLachlan (1949) used a colorimetric analysis method to analyse dissolved amounts of TCE in water, based on a modification of the Fujiwara pyridine–sodium hydroxide reaction. Fujiwara (1914) had observed a crimson colour when traces of trichloromethane (TCM; chloroform; $CHCl_3$) or trichloroacetic acid were added to a boiling mixture of pyridine and strong aqueous alkali. A review of the Fujiwara reaction by Seto and Schultze (1956) reports that other halogenated hydrocarbons may give a positive Fujiwara test under suitable conditions and that without proper modification the method is non-specific. They cite ten investigators from the 1930s-1950s who adapted the Fujiwara procedure. Lyne and McLachlan were not cited.

Lyne and McLachlan (1949) provide few details of their specific Fujiwara pyridine alkali reaction, but it appears to be the first application for analysing water samples. A number of citations do cite Lyne and McLachlan (1949), primarily for its analytical method (Love, 1951; Klein, 1957; Schollmeyer, 1960; Mancy & Weber, 1971). These publications concern media or environments other than groundwater. In contrast to many papers which adopted the Fujiwara method, Lyne and McLachlan (1949) did not utilise any instrumentation, which was being marketed in the 1940s, for measuring the colour reaction. Love (1951) notes that "*increasing use of instruments in the analysis of water is apparent. Photometers and spectrophotometers of various kinds have largely displaced visual observations in colorimetric analysis.*" The importance of spectrophotometers was later illustrated by Seto and Schultze (1956), who used the Fujiwara method on urine samples. Examination of their absorbance-concentration graph indicates a detection limit approaching *ca.* 1 µg/L. Camisa (1975) also used the Fujiwara method on water samples and indicated "*acceptable sensitivity (1 µg)*", but again raises reliability and specificity issues. These findings indicate it was possible to quantify occurrence of Fujiwara-reactive chlorinated solvents (TCE, TCM) to around µg/L levels in the 1950s, although unequivocal identification of contaminants was not possible.

Application of the Fujiwara method to water analyses by other workers in the UK is not apparent. Montgomery and Conlon (1967) provide examples of GC analysis for the estimation of sludge chlorinated-solvent content (potentially adaptable to water samples). They did not cite the Fujiwara method, but suggested an aggressive Stepanow reduction as an alternative. Lovelock, the inventor of the ECD (electron capture detector) widely used in GC analysis of chlorinated solvents (Lovelock, 1961), and an early pioneer of atmospheric chlorofluorocarbons research, was unaware of Lyne and McLachlan's work (personal communication, Lovelock, J.E.). There was, however, UK interest in the Fujiwara test in other areas, notably the rapid detection of racehorse doping by the sedative chloral hydrate (Moss & Rylance, 1966; Badcock, 2000). There was potentially more use, albeit with reservations, of the reaction in the US. Schaumburg (1990) reports that prior to 1975 "*the Fujiwara colorimetric method of TCE determination was commonly used*", although citations are unfortunately not provided. Camisa (1975) lists various shortcomings of the method, and Schaumburg (1990) notes the most important problem for water analysis was the inability of the Fujiwara method to distinguish TCE from other chlorinated solvents. Rivett *et al.* (2006) indicate that although Fujiwara-based analysis of water samples, particularly groundwater, failed to trigger a widespread recognition of the solvents problem, there still remains interest in the Fujiwara reaction for water analysis. Angel *et al.*'s (1987) work on Fujiwara reaction mechanisms (that had proved quite elusive) underpinned the development of a Fujiwara-based optrode [optical electrode] that automatically and specifically monitors TCM and TCE in water to concentrations below 1 µg/L (Burge & Hoffman, 2003). It remains the only colorimetric method available to monitor dissolved TCE at low concentrations.

Re-emergence of Lyne & McLachlan (1949)

Modern citations of Lyne & McLachlan (1949) include Colten & Skinner (1994, 1996), Colten (1998), Travis (1998, 2002a,b), Jackson (1999, 2003, 2004), Amter & Ross (2001, 2008), and Shifrin (2005). These authors are all located in North America with the exception of Travis, who is based in Israel. The earliest citations, from the mid 1990s, by Colten & Skinner, coincide with the passing of the last surviving author, Lyne, in 1996. Prior to this time, including the period in the 1970-80s when chlorinated solvent contamination of the environment was becoming more recognised, Lyne and McLachlan's work was unknown to practitioners who worked on groundwater contamination. Appreciation in the UK of Lyne and McLachlan's work occurred several years after the citations in the USA. A few UK-based workers were conversationally aware of the paper's existence, and Rivett *et al.* (2005, 2006) were the first UK authors to recognise the significance of Lyne & McLachlan's work in contaminated groundwater research – more than 55 years after the original publication.

Conclusions and relevance

Lyne and McLachlan (1949) is believed to be the world's earliest known publication concerning TCE (or chlorinated solvent) occurrence in groundwater. It appears to be a "one-off" publication on groundwater by these two UK authors, who at the time were Public Analysts working for several local authorities. The significance of their work for the contamination of groundwater only began to be recognised in the mid-to-late 1990s, in North America at least. The principal conclusion to be drawn is that Lyne and McLachlan failed to trigger any general recognition of the solvents-in-groundwater problem across the scientific, industrial, or regulatory communities. This unfortunate conclusion appears to be true at all levels – local, national and international. Their paper's message was never disseminated to, or acted upon by, a wider audience, and it is questionable whether the potential prescience of their early work was ever really apparent to Lyne and McLachlan themselves. The historic lack of contribution to foreseeability of the problem means that Lyne & McLachlan (1949) is expected to have a limited influence on present-day litigation that involves historic solvent pollution of groundwater.

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* The constituent societies of the Royal Society of Chemistry were:

- The Chemical Society (founded in 1841)
- The Society for Analytical Chemistry (founded in 1874)
- The Royal Institute of Chemistry (founded in 1877)
- The Faraday Society (founded in 1903).

The Society for Analytical Chemistry (formerly The Society of Public Analysts) was subsumed by the RSC's Analytical Division. See also: **Association of Public Analysts** http://www.publicanalyst.com/index.html

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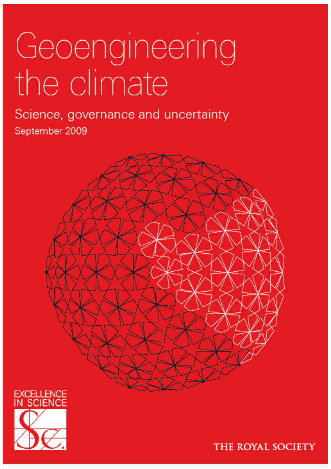
Royal Society report on geoengineering

A Royal Society study of geoengineering schemes for modulating the climate (see ECG *Bulletin* January 2009, p 35) was published in September 2009. A pdf of the report 'Geoengineering the climate: Science, governance and uncertainty' is available from the Royal Society web site, http://royalsociety.org/geoengineeringclimate/



Pharmaceuticals and sewage treatment

Sewage treatment works are a major defence for the environment against pharmaceuticals which are found in wastewater. Dr Roger Reeve from the University of Sunderland describes recent advances.

Pharmaceuticals in the environment

Concerns over pharmaceuticals in the environment have been growing since the 1990s. Kolpin *et al.* (2002) reported the presence of large numbers of pharmaceuticals and other organic compounds in environmental waters at sub-μg L^{-1} concentrations. The effect of pharmaceuticals on aquatic organisms is well-established (Hill *et al.,* 2005), and there is also the possibility of pharmaceuticals entering the food chain. Sex hormones and other steroids attracted early attention because of their endocrine-disrupting properties and ability to bioaccumulate, due to their hydrophobicity. Of current environmental concerns are the majority of pharmaceuticals, which are generally less hydrophobic than steroids. The decline in vulture population in Pakistan has been attributed to bioaccumulated residues of the relatively hydrophilic analgesic diclofenac (Oaks *et al.*, 2004).

Many investigations have confirmed that sewage treatment works are a source of the pharmaceuticals found in streams and rivers (e.g. Heberer, 2002; Roberts and Thomas*,* 2006; Kasprzyk-Hordern *et al.*, 2008; Choi *et al.*, 2008; Zhou *et al*., 2009). Treatment normally reduces the concentration of a pharmaceutical in the water, but a number seem resistant to the treatment, and in some cases an increase in concentration of the drug is found. This review discusses how the properties of pharmaceuticals and their metabolites affect their behaviour in the environment, and particularly during sewage treatment. Examples are taken from papers published in last two or three years. Earlier literature has been reviewed by Jones *et al.*, (2005) and Drewes, (2007). Recent reviews have covered the fate of pharmaceuticals in the environment and in water-treatment systems (Aga, 2008), and the removal of emerging contaminants including pharmaceuticals (Bolong *et al.*, 2009).

Pharmaceuticals entering the sewage-treatment system are largely from human usage. Other discharges into streams and rivers include those from veterinary usage. Veterinary antibiotics in the environment have recently been reviewed in this *Bulletin* (Bottoms, 2009).

Environmental concentrations of pharmaceuticals

The environmental concentration of a pharmaceutical is a function of the amount used and other factors such as **drug metabolism**, and **physicochemical properties**, which determine the fate of a drug in sewage treatment and in environmental degradation and reconcentration processes. Prescription data are sometimes used to estimate the quantities of drugs consumed, and hence released to the environment (Jones *et al.*, 2002). However, many common drugs are available without a prescription, and concentrations found in environmental waters often show little correlation with prescription data.

A view of the flood plain of the River Ouse at Northease near Rodmell, East Sussex, December 2009. *Pharmaceuticals are discharged into the River Ouse at the Scaynes Hill wastewater treatment works near Haywards Heath (Zhou et al., 2009). Photograph © Carole & Andrew Walters.*

Drug metabolism. Only a small proportion of a drug remains unchanged during its passage through the body (Kasprzyk-Hordern *et al.*, 2007; Winkler *et al.*, 2008). Phase I metabolism adds polar groups to the molecular framework. This increases aqueous solubility and allows excretion in urine. Metabolites can sometimes be found in greater concentration in environmental waters than the original drug. The main form of sulphamethoxazole in raw influent water is its metabolite *N*-acetylsulfamethoxazole (Göbel *et al.*, 2007). Metabolites usually have lower physiological activity than the parent drug, though for paracetamol a minor metabolite is the compound responsible for its toxic effects. Phase II metabolism forms conjugates in which the drug is coupled with a hydrophilic side-group. Paracetamol forms sulphate and glucuronide conjugates (Moffat *et al.*, 2004). Conjugation again increases the water solubility. It is possible for conjugates to break down during sewage treatment to regenerate the original drug and so increase its concentration in the effluent (Roberts and Thomas, 2006).

Physicochemical properties. The majority of drugs are either weak acids or weak bases. Because many of these compounds have a **dissociation constant (pK_a)** value in the region of 4-9 (Jones *et al.*, 2002), the ionisation of drugs will differ significantly in aqueous environments which have different pH values. Typically soft water has a pH of 5.5-7.0, hard water 7-8 and sea water 7.5-8.4. For an acid, the fraction remaining unionised, $f_{\mathrm{unionised}}$, can be calculated by

$$f_{unionised} = \frac{1}{(1 + 10^{pH - pK_a})}$$

Typical solubilities of the unionised forms are in the low mg L^{-1} range. The ionised form will have much higher solubility.

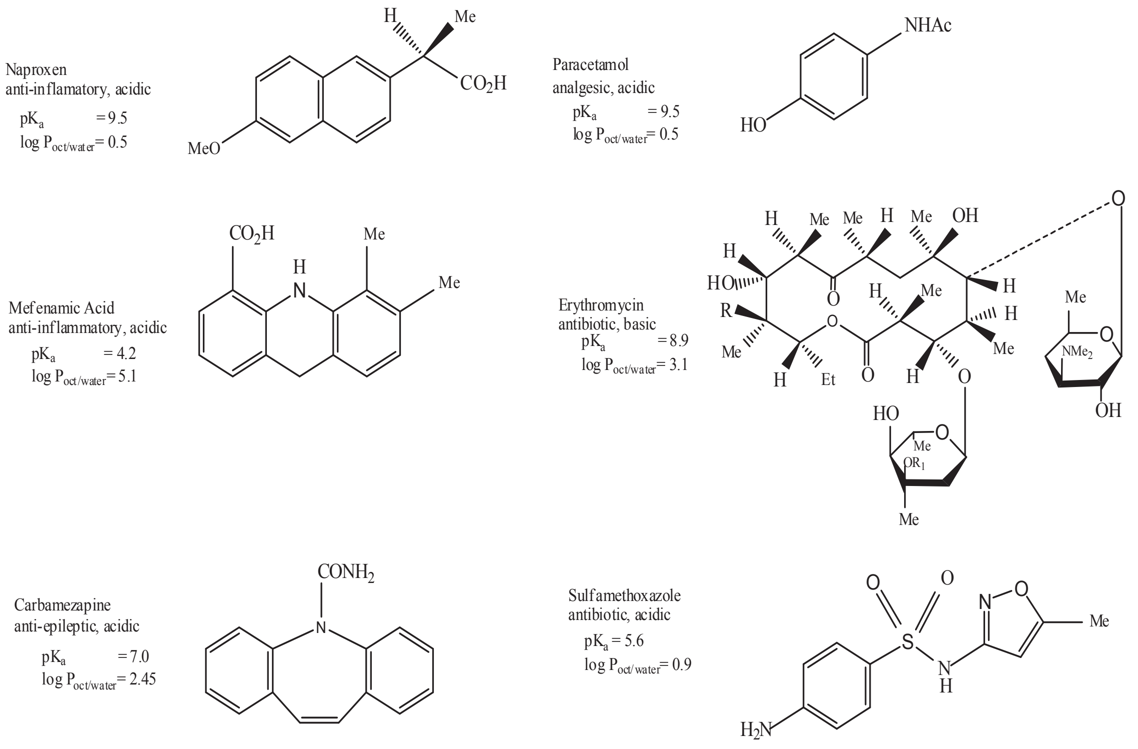
One of the mechanisms for pharmaceutical removal in sewage treatment is the sorption of hydrophobic or insoluble material onto solids and so will be pH dependent.

The **octanol/water partition coefficient**, K_{ow}, is used to estimate the bioconcentration of pollutants (Chiou *et al.*, 1977) or sorption of neutral organic compounds onto solid material (Jones *et al.,* 2005). Modification of K_{ow} to account for partial ionisation leads to a prediction of pH dependence of bioconcentration and sorption.

$$K_{\mathrm{mod}} = K_{ow} \cdot f_{unionised}$$

However, this approach was developed for non-polar pollutants, (e.g. *p,p'*–DDT, dioxins, PCBs), which partition by hydrophobic interaction. Even the neutral forms of drugs can be highly polar, leading to electrostatic and other interactions with solids (Radjenović *et al.*, 2009) and this may not have been taken into consideration in simple models.

Pharmaceuticals are often classified according to their therapeutic action. Representative pharmaceuticals are shown in **Figure 1** together with **dissociation constant** and **octanol/ water partition coefficient** data.



Naproxen
anti-inflamatory, acidic
$pK_a = 9.5$
$\log P_{oct/water} = 0.5$

Paracetamol
analgesic, acidic
$pK_a = 9.5$
$\log P_{oct/water} = 0.5$

Mefenamic Acid
anti-inflammatory, acidic
$pK_a = 4.2$
$\log P_{oct/water} = 5.1$

Erythromycin
antibiotic, basic
$pK_a = 8.9$
$\log P_{oct/water} = 3.1$

Carbamezapine
anti-epileptic, acidic
$pK_a = 7.0$
$\log P_{oct/water} = 2.45$

Sulfamethoxazole
antibiotic, acidic
$pK_a = 5.6$
$\log P_{oct/water} = 0.9$

Figure 1: *Representative pharmaceuticals found in waste water*

Many pharmaceuticals have chiral centres, and therapeutic activity is enantiomer-specific.

The enantiomeric ratio of a drug may change in the environment and during sewage treatment (Buser *et al*., 1999; Matamoros *et al*., 2009), altering its potential effect on organisms.

Most pharmaceuticals contain aromatic groups which absorb UV radiation. Ozone will attack any carbon-carbon multiple bond. UV photolysis and ozonolysis are two methods for degrading pharmaceuticals and are often used in tertiary sewage treatment.

Sewage treatment

Pharmaceuticals and their metabolites are predominantly excreted in urine though they may also be present in faeces (Winkler *et al*., 2008). Input concentrations to sewage treatment plants are usually less than 1-2 µg L^{-1} with higher concentrations for more common drugs such as paracetamol (Miège *et al*., 2009). Sewage treatment processes are graded as **primary**, **secondary** and **tertiary treatment**. Most sewage plants have primary and secondary treatment. Tertiary treatment is usually a method for the removal of contaminants which are specific to a given location.

The aim of sewage treatment is to produce an effluent with as low an organic content as possible, a low suspended-solid content and with pathogenic micro-organisms removed. Discharge concentrations may be set for individual chemicals. Sewage sludge is produced as a waste and is commonly disposed by landfill or is spread on land as a soil conditioner. Both can be additional routes for the pharmaceuticals to re-enter the environment.

Two operating parameters have been found useful for plant comparison: **hydraulic retention time** (**HRT**) and **solids retention time** (**SRT**). An accurate estimation of HRT is also necessary in the experimental determination of removal efficiencies (Zorita *et al*., 2009) as input and effluent samples need to be matched. Terzic *et al*. (2008) have suggested that some results showing increases in concentration during treatment processes may be due to sampling inaccuracy.

Primary treatment

This is the removal of floating and suspended solids such as wood, paper and faecal matter, which would disrupt later stages of the treatment, and comprises screening and sedimentation. Hydrated lime, aluminium sulphate or iron salts may be added to promote the sedimentation. One investigation indicated that drug concentrations are lowered during primary treatment and by implication are removed with the solid matter (Zorita *et al.*, 2009). This was correlated with their low K_{ow}. However, no elimination was found for sulfonamides, macrolides and trimethoprim (Göbel *et al*., 2007) or for a range of anti-microbials (Peng *et al.*, 2006).

Secondary treatment

Organic material is degraded under aerobic conditions using populations of micro-organisms incorporated into activated sludge and/or membrane bioreactors. Loss of pharmaceuticals can be either by degradation or sorption onto sewage sludge. Santos *et al.* (2005) studied four sewage plants with primary and activated sludge secondary treatment: 90% removal was achieved for ibuprofen, *ca.* 60% for naproxen but below 26% for carbamezapine. Peng *et al.* (2006) found that activated sludge could remove > 85% of several antimicrobials. Poor removal was found for naproxen and ketoprofen, both amide-type pharmaceuticals (Nakada *et al.*, 2006). A plant with primary treatment, activated sewage sludge, and final clarification (Gómez *et al.*, 2007) showed >70% removal for a wide range of drugs except diclofenac (59%) and carbamezapine (20%). Carballa *et al.* (2007) found no elimination of carbamezapine**.**

Joss *et al.* (2006) investigated the action of activated sewage sludge and membrane bioreactors in batch experiments. Pharmaceuticals were grouped according to the first-order degradation rate constants derived from this study. The results broadly correlated with results from sewage plants, and showed a low rate for diclofenac. The highest rate was for paracetamol. Non-correlation was attributed to the pres-

Scaynes Hill wastewater treatment works.

Image copyright Nigel Freeman: http://www.geograph.org.uk/photo/24707 ence of conjugates. Implications are that dilution of the input stream (e.g. by rainwater) would lower the degradation rate, and that treatment in small compartments rather than a single large compartment would improve the degradation. Increased HRT would also increase degradation. Choi *et al.* (2008) studied four sewage plants with activated sludge treatment over a range of flow and input concentrations. Cimetidine, sulphamethoxazole and carbamezapine were poorly removed under all conditions.

Maurer *et al.* (2007) compared batch experiments for the removal of β-blockers with results from two sewage treatment plants. The performance improved with increasing HRT, and the elimination appeared to be by biological degradation rather than sorption onto sewage sludge. Sorption coefficients did not correlate with $K_{ow.}$ This was attributed to ionic interactions with the solid. Jones *et al.* (2007) studied an activated-sludge plant with nitrifying and denitrifying zones. Elimination rates were *ca.* 90% for ibuprofen, paracetamol, salnutamol and methanamic acid. Mass balances indicated removal by biological degradation rather than sorption onto the sewage sludge. Gulkowska *et al.* (2008) compared plants with primary and secondary treatment and chemically-enhanced primary treatment for antibiotic removal. The highest removal efficiencies were with antibiotics, which were readily adsorbed onto particulate matter. Increased HRT appeared to increase the removal efficiency.

Terzic *et al.* (2008) gave a summary of the behaviour of pharmaceuticals in over 70 wastewater treatment plants and a detailed study of one plant biological treatment plant. Effluent concentrations exceeded input concentrations for atenelol, diclofenac, trimethoprym, arithromyan and erythromycin, and only ibuprofen had >95% removal efficiency. Increasing concentrations of propranolol, tamoxifen and methanamic acid have been found by Roberts and Thomas (2006). Radjenović *et al.* (2009) compared the removal of conventional activated sludge with pilot-plant advanced-membrane bioreactor treatment. Enhanced removal was found for most drugs with the membrane bioreactor, but carbamezapine and hydrodichlorothiazide had less than 10% removal in each process. Twenty out of the twenty-six pharmaceuticals were detected in the sewage sludge.

Several recent papers have investigated specific pharmaceuticals which cause problems or those which have not been given much attention: Zhang *et al.* (2008); Stülten *et al.* (2008); Leclerq *et al.* (2009); Scheurer *et al.* (2009).

Miège *et al.* (2009) have compiled a database of removal efficiencies of plants with primary and secondary treatment. Statistical analysis indicated that activated sludge with nitrogen treatment and membrane bioreactors were the most efficient. The KNAPPE project, part of the EU Sixth Framework Programme (Touraud, E., 2008) concluded that the secondary treatment plant design is not a major factor. More important considerations are operating parameters such as SRT and HRT.

Tertiary treatment

Disinfection either by UV, chlorination or ozonolysis is the most common tertiary-treatment process. The plants may not be operated continuously. Northumbria Water (UK) has applied to turn off UV treatment on six of its plants outside the bathing/watersport season (Environment Agency, 2008). Chlorination of the treatment plant on the River Rakkolanjoki (Finland) is only applied May –September (Vieno *et al*., 2007). Klavarioti *et al*. (2009) reviewed laboratory or pilot-plant scale disinfection methods alongside these current processes. Other tertiary-treatment processes include phosphate removal and sand filtration (Göbel *et al.,* 2007; Zorita *et al.,* 2009), and sewage application to land (Gielen *et al.*, 2009).

UV treatment. 254 nm mercury lamps are used. Other wastewater components can absorb the radiation, and the radiation may not be able to penetrate solids. Roberts and Thomas (2006) found that during UV tertiary treatment there was a decrease in concentration of all pharmaceuticals studied except for erythromycin, the only compound without a UV-absorbing aromatic ring. The maximum removal efficiency was *ca.* 70%. However, UV treatment may not completely destroy the molecular framework. Miao *et al.* (2005) found an increase in concentration of carbamezapine metabolites, possibly due to conjugate destruction. Kim *et al.* (2009) compared UV and UV/H_2O_2 treatment. Increased destruction was found with UV/ H_2O_2 for all pharmaceuticals including erythromycin. Earlier work had shown similar improved destruction of carbamezapine. Laboratory studies by Yuan *et al*. (2009) showed improvement for ibuprofen, diphenylhydramine, phenazone and phenytoin.

Chlorination. Vieno *et al.* (2007) have compared plants with primary, secondary and a range of tertiary treatment including coagulation, chlorination and polymer addition (HRT 1.5-17.5 hr). Carbamezapine was not removed, whereas > 85% fluoroquinolines were eliminated. Four treatment plants with different technologies (conventional sewage sludge, oxidation ditches, bioreactors with UV treatment and chlorination, lagoons) have been studied by Ying *et al.* (2009). Biodegradation seems the main mechanism rather than sorption onto sludge. There was little removal of diclofenac in any of the processes. Xu *et al.* (2007) studied antibiotics in four plants with UV, chlorine and no disinfection. The least effective was the plant with no disinfection. In contrast to removal mechanisms for most other pharmaceuticals, the removal of hydrophobic fluoroquinolines was attributed to absorption on sewage sludge.

Ozonation. Nakada *et al.* (2007) have studied the effect of ozonation in combination with sand filtration, and correlated the removal efficiency with chemical structure. Compounds with a double bond or aromatic ring were readily removed (over the whole treatment process > 80%), whereas compounds with amide structures (e.g. carbamezapine, diethyltoluamide) were resistant. Sand filtration had a variable effect but appeared to correlate with drug hydrophobicity.

Sludge disposal

Over 8.1 million tons of sewage sludge are produced in the EU each year; 21% is disposed of on land in Sweden (Eriksonn *et al.*, 2008) and 65% in Spain (Carbonell *et al.*, 2009). 35-45% is disposed as landfill (Touraud, 2008). There has long been concern over the possibility of heavy metals re-entering the food chain from sewage sludge application, and of the presence of pathogenic micro-organisms. This concern now includes pharmaceuticals. Drainage from sewage sludge in landfill can contaminate groundwater. Díaz-Cruz *et al.* (2003) have summarised the behaviour of drugs in soils, sediments and sludge. Eriksson *et al.* (2008) found twenty pharmaceuticals in sewage sludge with 128 others potentially being present. Typical concentrations found are in the ng g^{-1} range (Barron *et al.*, 2008; Sponberg and Witter 2008, Radjenović *et al.*, 2009). After application to soil, there is evidence of degradation, but successive reapplication could increase drug concentrations significantly. A recent comprehensive review of organic contaminants in sewage sludge (Smith, 2009) has concluded that the main concern for pharmaceuticals in the environment is the development of antibiotic resistance in soil bacteria.

Topp *et al.* (2008) have studied surface run-off following surface application and sub-surface injection of biosolids. Subsurface application effectively eliminates surface run-off. Edwards *et al.* (2009) studied the effect of biosolids applied to land and their concentrations in tile drainage systems (removing excess water from the soil subsurface). Carbamazapine, sufamethoxazole and naproxen were detected in the drainage water. Sabourin *et al.* (2009) investigated the transport potential in surface run-off, correlating this with K_{ow}. Pharmaceuticals which with log $K_{ow} < 2.45$ were readily mobilised and those with log $K_{ow} > 3.18$ had little transport potential. Kinney *et al.* (2008) have studied the uptake into earthworms in a field treated with biosolids. Carbamezapine was detectable in the original bio-solid but could not be detected in the treated soil or in the earthworms.

Summary

There is some correlation of drug degradation rates with their physicochemical properties. But differences in performance of individual sewage plants (operating factors HRT and SRT, and plant design) need to be taken into consideration. A high hydraulic retention time, and a plant design which encourages a diversity of bio-organisms, promote the efficient removal of drugs. There is also an increasing awareness of the need for tertiary treatment.

A wide range of pharmaceuticals is used medicinally. Hence no single sewage treatment method is suitable for all drugs. A number of individual drugs, e.g. carbamezapine and diclofenac, appear to have low removal efficiencies in primary and secondary treatment regardless of plant design. UV treatment is effective for a large number of pharmaceuticals; addition of H_2O_2 shows promise for increasing rates of degradation. Although loss by adsorption on sludge appears to be a minor factor in the removal of many pharmaceuticals in sewage treatment, increased use of sewage sludge as a soil conditioner is an additional route for pharmaceuticals to contaminate soil, with further leaching into groundwater.

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First mercury reference laboratory is established in Southern Africa

With its reliance on coal as an energy source, South Africa has established a dedicated resource to monitor for mercury released by combustion, and other routes, into the environment, as Project Leader **Vernon Somerset** explains.

Monitoring trace metals in the environment

Heavy metals are some of the most widespread of environmental pollutants. They originate predominantly from anthropogenic activities, such as mining, agriculture, industrial wastewater and effluent, urban runoff, irrigation with treated wastewater, and atmospheric deposition. Through these activities, large amounts of heavy metals are released into fluvial systems and can be transported along hydrogeological gradients for hundreds of kilometres in relatively short times. The release of heavy metals from these sources can occur both in dissolved and in particulate form. The continuous assessment and monitoring of trace metals in the environment is essential to gain a better understanding of the individual and interactive effects of the trace metals in water resources (*i.e.* rivers, lakes, dams, etc.) worldwide. National and international legislation have set limits for the maximum allowable concentrations of various trace metals in the air, water and aquatic ecosystems. In order to regulate and to comply with legislation, routine estimations of the amounts of metals in the environment are needed. Monitoring and measurements of heavy metals in the environment also require accredited sample collection procedures and analytical techniques (Somerset, 2009a).

Exposure sources and toxicity of mercury

Mercury in the environment has been a concern worldwide for many decades. Exposure of the human population to mercury can occur directly through the application of mercury and mercury compounds, and indirectly by eating fish and other aquatic food which have bioaccumulated methylmercury (Clevenger *et al.*, 1997; Dolci *et al.*, 2006; Peng *et al.*, 2005; Moreda-Piñeiro *et al.*, 2002). Mercuric sulphide has been used as a remedy for skin and eye complaints, and metallic mercury and mercuric chloride have also had medicinal applications in the past. Other applications of mercury and its compounds include diuretics, dental amalgam fillings, and antiseptics (Bontidean *et al.*, 2004; Hobman and Brown, 1997; Hobman *et al.*, 2000; Maggi *et al.*, 2009). Mercury pollution from anthropogenic sources is common in industrialised countries, leading to direct pollution of soil and indirect contamination of groundwater and food sources (Bontidean *et al.*, 2004; Pan-Hou *et al.*, 2001; Di Natale *et al.*, 2006). Sources of mercury pollution include fossil fuel combustion, calcination of pyrites, or the releases from former industries (e.g. chlor-alkali plants), all of which result in the liberation of large amounts of mercury and its compounds into the biosphere (Peng *et al.*, 2005; von Canstein *et al.*, 1999; Krishnan and Anirudhan, 2002).

Elemental and mercuric mercury [Hg(0) and Hg^{2+}] are poorly absorbed from the gastrointestinal tract, but Hg(0) is readily absorbed by inhalation. Methylmercury compounds are absorbed through the skin, by ingestion and by inhalation, and have long retention times in the body. Mercurous salts are probably oxidised to Hg^{2+} in the gastrointestinal tract before absorption. The speciation of mercury compounds [Hg(0), Hg^{2+}, RHg^{+}, RHgR'] influences their distribution and hence their toxicity. The main target organ for inhaled mercury vapour and methylmercury in primates is the central nervous system, while the kidney is the target organ for mercuric mercury in all species. Methylmercury is mainly eliminated in faeces with partial demethylation; the predominant route of excretion of Hg^{2+} is urinary (Clarkson, 1997).

Determination of mercury

Classical methods and techniques for determining mercury in the environment include atomic adsorption spectroscopy (AAS), atomic fluorescence spectroscopy (AFS), atomic emission spectroscopy (AES), inductively-coupled plasma mass spectroscopy (ICP-MS), and capillary electrophoresis (CE). These are well-established methods and are characterised by low detection limits (i.e. 0.02 ppb for AAS; 0.001 ppt for AFS; 0.01 ppt for AES and 0.08 ppt for ICP-MS) (Bontidean *et al.*, 2004; Emteborg *et al.*, 1996; Cossa *et al.*, 1995; Jamoussi *et al.*, 1995; Hintelmann *et al.*, 1995; Peng *et al.*, 2005; Liu and Lee, 1998; Buffle and Tercier-Waeber, 2005).

Alternatives to the classical methods and techniques include electrochemical methods of mercury determination (e.g. ion-selective electrodes (ISE); anodic stripping voltammetry (ASV); potentiometric stripping analysis (PSA); current stripping chronopotentiometry (CSP); and differential pulse voltammetry (DPV). These methods are characterised by higher detection limits (i.e. 0.2 ppt for ASV; 0.5 ppb for PSA; 0.1 ppb for CSP and 2 ppt for DPV. However, they provide the opportunity for on-site screening for mercury in the environment (Bontidean *et al.*, 2004; Shatkin *et al.*, 1995; Wang and Tian, 1993; Beinrohr *et al.*, 1996; Ugo *et al.*, 1995; Dolci *et al.*, 2006).

Figure 1: *Water, sediment and biota samples from specific rivers were taken to the CSIR Mercury Reference Laboratory in Stellenbosch for sample preparation, digestion and analysis for total mercury and methylmercury concentrations, respectively*

Mercury in the South African environment

In order to investigate and understand the behaviour of mercury in the South African environment, the Council for Scientific and Industrial Research (CSIR) has established the first Mercury Reference Laboratory at the CSIR in Stellenbosch, Western Cape, South Africa. The laboratory forms part of the Water Ecosystems and Human Health research group, within the Natural Resources and the Environment (NRE) research sector in the CSIR. With this laboratory in operation, a team of CSIR researchers were able to conduct a national survey of mercury in the country's surface water resources. This investigation was conducted at over sixty sampling sites in all nineteen of South Africa's water management areas.

Through this investigation we have gained a better understanding of the condition of our country's water and atmosphere in terms of the mercury released into the environment. The collected data also allowed us to assess how bioaccumulation occurs in the national freshwater aquatic food chains, and thereby determine the impact on the associated water resources and human health. Mercury in South Africa is typically released into the environment through coal combustion, waste incineration, base-metal smelting, artisanal gold production, and cement production. South Africa relies primarily on coal to produce energy at its many coal-fired power stations, where mercury is potentially released into the environment at our coal-fired power plants. These mercury emissions then enter our water ecosystems through wet and dry deposition, making it crucial to monitor and manage mercury in the South African environment. Results obtained from the national survey reveal elevated concentrations of total mercury (TotHg) and methylmercury (MeHg) at specific sites. These sites are located in the vicinity of coal-fired power plants, in an area impacted by artisanal gold mining activities, and at a previously Hg-contaminated area (Somerset *et al.* 2009b).

Analytical facilities and equipment

The Stellenbosch facility has state-of-the-art equipment for the analysis of water, sediment, biota (invertebrates and fish) and air samples for total mercury and methylmercury. Using the methods recommended by the US Environmental Protection Agency, TotHg and MeHg in water samples can be analysed to the nanogram per litre (or ppt) range, and in sediment and biota samples to the nanogram per gram (or ppb) concentration range.

The following instruments are available in the laboratory:

- A Tekran® Model 2500 Cold Vapour Atomic Fluorescence Spectrophotometric (CVAFS) detector that is used with an analytical system capable of producing mercury vapour in an Argon inert gas stream, followed by detection with the instrument.
- A Tekran® Series 2600 system that allows the analysis of ultra-trace levels of TotHg in water (or liquid) samples.
- A Tekran® Model 2537 Mercury Vapour Analyzer that provides continuous analysis of total gaseous mercury (TGM) in air at sub-ng/m^3 (parts per trillion (ppt) and parts per quadrillion (ppq)) levels.
- A Milestone® Direct Mercury Analyser (DMA-80) for the determination of TotHg in sediment and biological tissue, allowing effortless of solid samples with no sample preparation.

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Has the vision of Arthur Symons been conserved at Loe Pool?

Are the objectives set by the Loe Pool Management Forum (LPMF) being achieved? Leo Salter reported on the LPMF in the July 2003 issue of the ECG *Bulletin*. **Victoria Holmes**, from Cornwall College, provides an update on the progress to rehabilitate Loe Pool to an ecologically stable condition.

Loe Pool. Loe Pool (**Figure 1**) is the largest natural freshwater lake in Cornwall with a surface area of 0.56 km^2, and the main inflow, the River Cober, has a drainage area of 54 km^2. This shallow coastal lake has considerable amenity value (30,000 visitors p.a. (National Trust, 1998)) and is of national significance, which is reflected by its designation as a Site of Special Scientific Interest and County Wildlife Site (Dinsdale, 2009).

Figure 1: *Loe Pool, Cornwall. Source: National Trust*

Nitrogen and phosphorus inputs. Concentrations of nitrogen and phosphorus have been elevated in the Pool, possibly for decades, fuelling proliferation of algae (*Microcystis aeruginosa* and *Hydrodictyon reticulatum*) and therefore the demise of submerged macrophytes and the populations of coarse fish. The Pool suffers from advanced euthrophication, with predominant inputs of phosphorus sourced from the Helston Sewage Treatment Works (STW) and the STW located at the Royal Naval Air Station (RNAS), Culdrose, plus nitrogen inputs from diffuse sources (mainly agriculture).

Review of the Loe Pool Catchment Management Project. In 1998, project targets and objectives were defined by the Loe Pool Catchment Management Project (LPCMP) and these remain largely unchanged in 2009. Since the introduction of the Water Framework Directive, Loe Pool is subject to an extensive programme of long-term monitoring, which will allow the progress towards the Project's targets to be assessed for the first time. The findings from the latest LPCMP review (**Figure 2**, Dinsdale, 2009) show a fourfold reduction in the average annual total phosphorus concentration of Loe Pool between 1997 and 2004. This reduction coincides with the installation of tertiary treatment (phosphorus stripping) at the Helston STW in 2003 (Urban Wastewater Treatment Directive) and work to tackle pollution from agriculture (1999 to 2009) (Dinsdale, 2009).

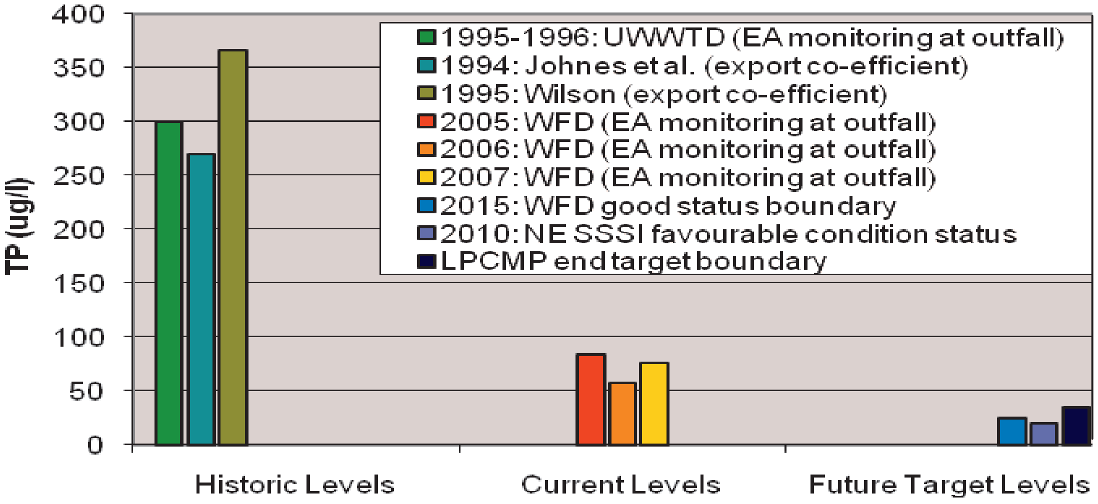
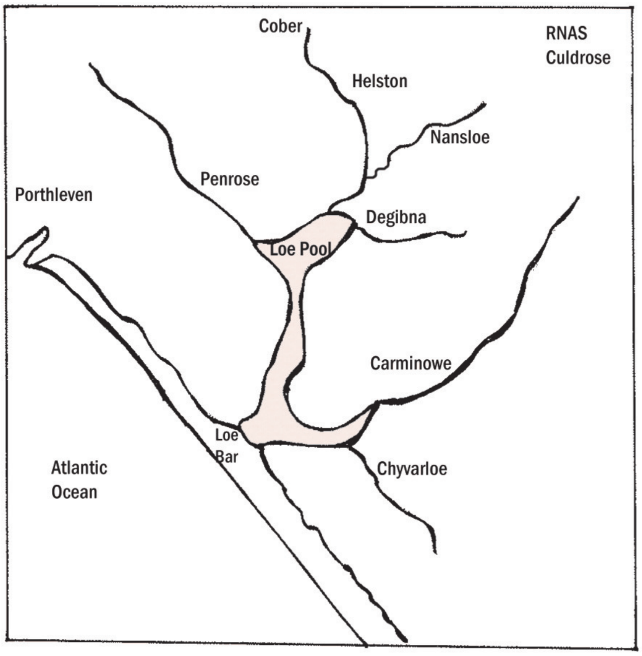


Figure 2: *Historic, current and target total phosphorus (TP) concentrations for Loe Pool (Dinsdale, 2009)*

The reduction in total phosphorus is extremely encouraging as it indicates there is currently little remobilisation of phosphorus from the benthic sediments in the Pool, which is in contrast with findings from other lake restoration schemes (Marsden, 1989; Phillips, 2005). Levels of phosphorus within the sediment could potentially have become a significant source of phosphorus during the lake rehabilitation (Wilson & Dinsdale, 1998). However, it was predicted that iron present in the sediment from historic mining activities in this area of Cornwall, would absorb the sedimentary phosphorus (Olosundé, 2002). The data appear to support this theory.

High peaks in the concentrations of total phosphorus were found in Nansloe Stream and Chyvarloe Stream, which flow into Loe Pool (see **Figure 3** for locations) (BREY Services, (2009). These peaks could not be consistently correlated with incidences of high rainfall (McCaffrey, 2008), but are thought to be linked to agricultural activities.



Schematic of tributaries flowing into Loe Pool

Figure 3: *Six watercourses which flow into Loe Pool*

Phosphate levels are high and consistent in Carminowe Stream, where the primary source of phosphorus is likely to be RNAS Culdrose Sewage Treatment Works. The majority of phosphorus entering Loe Pool is in the biologically available form of orthophosphate (BREY Services, 2009). The largest proportional contribution to the total phosphorus in Loe Pool was from the River Cober (61%), despite this source having a relatively low phosphorus concentration. Carminowe Stream and Nansloe Stream also contribute phosphorus, and high nitrate and ammonia concentrations were found in a few of the tributary streams (McCaffery 2008; BREY Services, 2009).

Work for the next quinquennium. The Loe Pool Catchment Management Project remains at the first step of a three-stage rehabilitation: (1) reduction of nutrient loading; (2) biomanipulation; (3) recovery of water plants. Management for the next five years needs to continue restricting the sources of phosphate and other nutrients within the catchment area (Dinsdale, 2009). One of the priorities for 2009-2014 will be the reduction in the export of phosphorus from sewage works at RNAS Culdrose, ideally through the installation of a phosphate removal plant. Currently, the Environment Agency is assessing the evidence to see if there is sufficient cause to modify the consent to discharge. Another priority is the reduction of agricultural sources of nutrients, sediments and pesticides. This goal will be achieved through the Rural Catchment Initiative. A 'nutrient budget' will also be established to account for the various nutrient sources of phosphorus within the catchment. Finally, two outcomes from the current LPCMP Review (Dinsdale, 2009) have been the rehabilitation of the River Cober following its reprofiling to reduce a flood risk at Helston, and the adaptation of a water regime to allow the re-establishment of submerged vegetation in Loe Pool.

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December 2009

Forthcoming Symposium

King Coal: future prospects for growth, use and clean technologies

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RSC Environmental Chemistry Group - 2010 Distinguished Guest Lecture & Symposium

A half-day meeting to be held in the Library of the Royal Society of Chemistry, Burlington House, Piccadilly, London on Wednesday 24th March 2010, from 12.00 noon onwards.

The 2010 ECG Distinguished Guest Lecturer will be **Professor James Harrison** (British Coal Utilisation Association)

PROGRAMME

12.50 Chairman's Introduction: Dr Leo Salter (Chair, ECG)

13.00 Dr Douglas Parr (Greenpeace UK): *Risks of, and alternatives to, new Coal*

13.45 Nigel Yaxley (CoalImp (Association of UK Coal Importers)): *World coal and the imperative for CCS*

14.30 **Environmental Chemistry Group 37th Annual General Meeting**

15.00 Professor Stuart Haszeldine (University of Edinburgh): *Carbon capture and geological storage: Silver bullet, or broken bridge to the future?*

15.45 Introduction to the 2010 ECG Distinguished Guest Lecture and presentation of the ECG DGL Medal

15.50 **RSC Environmental Chemistry Group Distinguished Guest Lecture for 2010**: Professor James Harrison, British Coal Utilisation Association) *Advances in the technology of the use of coal*

16.50 Open Forum

17.15 Close

A buffet lunch will be served at 12.00 noon. Coffee/Tea will be served at 14.30

The nearest tube stations are Green Park and Piccadilly Circus

Admission is by ticket only. In order to register for this meeting, please complete the slip below and return to Dr Leo Salter by post, email or fax (see details below). There is a charge of £25 for members of the ECG and £50 for non-members of the ECG (£25 concessions, i.e. student/unwaged (proof required)). Cheques should be returned with the slip (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. Five places are reserved free for retired members; these will also be allocated on a first-come, first-served basis.

ROYAL SOCIETY OF CHEMISTRY, ENVIRONMENTAL CHEMISTRY GROUP

Thirty-seventh Annual General Meeting, 24th March 2010 and Distinguished Guest Lecture & Symposium *King Coal: future prospects for growth, use and clean technologies*

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Dietary/access requirements:

Please send to: Dr Leo Salter, Opie, Cornwall College, Pool, Redruth, Cornwall TR15 3RD
leo.salter@cornwall.ac.uk Fax 01209 616230

……

Biographical details of the speakers

Risks of, and alternatives to, new coal

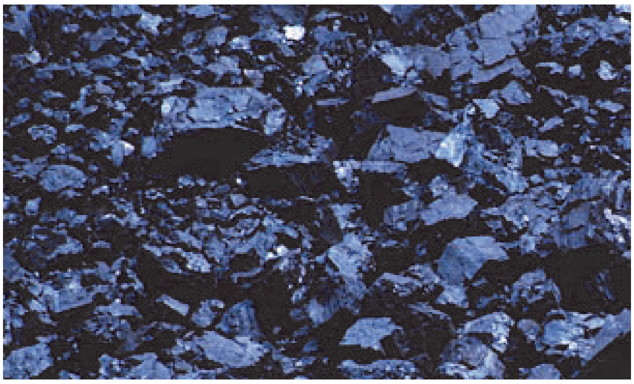
Dr Douglas Parr – Chief Scientist and Policy Director, Greenpeace UK

Dr Douglas Parr is Chief Scientist and Policy Director at Greenpeace UK, looking after the science and political lobbying functions. Currently working on climate change policy in the power, heat and transport sectors, Dr Parr has previously worked on a number of issues including GM crops, chemicals policy, green refrigeration, marine conservation, biofuels and nuclear power. He obtained a DPhil in Atmospheric Chemistry from Oxford University in 1991.

World coal and the imperative for CCS

Nigel Yaxley – Managing Director, CoalImp (Association of UK Coal Importers)

Nigel Yaxley is the founder and Managing Director of CoalImp, the Association of UK Coal Importers. Since 2006 he has developed his consultancy business in the coal and energy field, with clients including UK and international mining businesses, UK companies involved in power generation and equipment manufacture, trade unions, the UK Government and the European Commission. Nigel joined the coal industry in 1977 after graduating in Physics from Cambridge University.



He moved to UK Coal in 1995 on privatisation of the industry and was Marketing Director until end-2005. From 2005 to 2007 he was President of Euracoal, which represents the interests of European producers and importers on the European stage, and is now Chairman of Euracoal's Market Committee.

Carbon capture and geological storage: Silver bullet, or broken bridge to the future?

Professor Stuart Haszeldine – Professor of Geology, University of Edinburgh

Stuart Haszeldine is a Professor of Geology at the University of Edinburgh. His research examines carbon capture and storage, in the context of changing climate, energy generation, and use. He co-leads the UK's largest university research group for CO_2 storage (at Edinburgh, Heriot-Watt and British Geological Survey at Edinburgh) www.geos.ed.ac.uk/sccs/, and is co-leader of the academic UK Carbon Capture and Storage Consortium www.geos.ed.ac.uk/ccs/. He was CCS lead on UKERC phase 1 and a technical advisor to the House of Commons Science and Technology Committee on CCS in 2006, and still provides advice to UK and Scottish Governments. www.geos.ed.ac.uk/homes/rsh; www.geos.ed.ac.uk/sccs/

Advances in the technology of the use of coal

Professor James Sumner Harrison – Chairman of the British Coal Utilisation Association: the 2010 ECG Distinguished Guest Lecturer

In most developed countries, coal has made a major contribution to the supply of the energy to support that development. Coal will continue to play an important part for the foreseeable future. However, the use of coal has been faced with increasing challenges to improve its performance and to deal with the demands of the environment. The technology of using coal and its products has progressively responded to these challenges, firstly by improving the efficiency of its use and more recently by dealing directly with the pollutants that are produced during combustion or conversion. The advances have been made partly by pragmatic step-by-step improvements in engineering practice, but in more recent years by a greatly improved scientific understanding of the nature of coal and of the processes involved in its utilisation.

Professor Harrison was born in Lancashire and educated at the Royal Grammar School Guildford and Loughborough College. He graduated at Loughborough and London University. He has been a Euro Engineer since 1990 and a Fellow of the Royal Academy of Engineering since 1994. He is a visiting Professor at Leeds University in the Energy & Resources Institute. Professor Harrison is Chairman of the British Coal Utilisation Association. He has been President of the Institute of Energy, and Chairman of the National Society for Clean Air and Environmental Protection. He was instrumental in setting up IEA Clean Coal Centre, the IEA Greenhouse Gas R&D Programme and a co-founder of the Coal Research Forum. He has served on the European Commission sub-committee for Energy Research and Development and on advisory committees of the UK Government. He has given evidence on the greenhouse effect and on clean coal technology to Select Committees of the Commons, Lords and the European Parliament.

Professor Harrison served on technology review committees of the International Energy Agency and he edited the IEA publication on Clean Coal Technology. He has been a member of several Executive Committees of IEA projects and was Managing Director of IEA Coal Research.

Since retiring as the Director of the Coal Research Establishment for British Coal, he has maintained his interest in environmental aspects of energy use and in the role of energy technology in contributing to the solution of developmental and environmental problems. He is a contributor to policy on these matters to the Institution of Chemical Engineers and Chairman of their Subject Group on Energy Conversion Technology. He was a founder of the non-governmental organisation, the Centre for Business and the Environment, and represented them at many United Nations meetings on climate change.

Book review

Air Quality in Urban Environments

Editors: R. M. Harrison and R. E. Hester, The Royal Society of Chemistry, Cambridge, UK, 2009
ISBN: 978-1-84755-907-4 (Hardback); pp xii + 162; £54.95

Air Quality in Urban Environments is the 28th volume in the RSC Series, 'Issues in Environmental Science and Technology'. Related previous titles include: *Air Quality Management* (No. 8); *Air Pollution and Health* (No. 10); and *Transport and the Environment* (No. 20). The seven chapters in this latest volume, edited by Professors Ronald Hester (York) and Roy Harrison (Birmingham), provide a comprehensive overview of the issues within urban air quality, including sources, health effects, dispersion and policy response.

The opening chapter, by Ole Hertel (NERI) and Michael Evan Goodsite (Aarhus), compares urban air pollution throughout the major cities of the world. The authors highlight the predominance of traffic emissions, contributions of trans-boundary pollutants, and the acute levels of exposure experienced in mega-cites, particularly in developing nations These levels are a stark contrast and valuable perspective for those of us managing concentrations that are at least within sight of the air quality objectives! The chapter also introduces the inherent complexities introduced by geography, topography and meteorology, the final point of which is taken up and expanded on in the following chapter by Jennifer A. Salmond (Auckland) and Ian G. McKendry (British Columbia). This second chapter discusses the local, urban and regional-scale atmospheric processes that affect pollutant transport and dispersal, the complex feedback mechanisms that make street-level concentrations difficult to predict, and the potential of informed urban design to reduce pollutant build-up.

In the third chapter, William Bloss (Birmingham) focuses on these complex chemical processes in the urban atmosphere, specifically the short-timescale reactions arising from traffic emissions and uncertainties in the current scientific understanding.

While the majority of urban air-quality problems result from road traffic, higher concentrations of some pollutants may also be experienced by underground commuters around the world, with unknown health implications, according to Imre Salma's (University of Eotvos) report in Chapter four.

Unregulated indoor exposure to air pollutants may be a dominant contributor to human health insults. In the fifth chapter, Sotiris Vardoulakis (London School of Hygiene and Tropical Medicine) provides a review of personal exposure assessment techniques which, he argues, should complement ambient air quality limit values, exposure reduction objectives and vehicle emissions and other standards in targeting air pollution in indoor and outdoor environments.

Robert L. Maynard (HPA) updates us, in the penultimate chapter, on the current research into the health effects of specific pollutants: particulate matter, nitrogen dioxide, sulphur dioxide, ozone, carbon monoxide and carcinogens, such as benzene, 1,3-butadiene, PAHs and arsenic. Key findings suggest that, contrary to the message conveyed by the setting of air quality objectives, there is no threshold of effect for many common pollutants; that long-term exposure to particulate matter leads primarily to cardiovascular, rather than respiratory, disease; and that ultrafine, or nanoparticles, may be the most toxicologically active (though the epidemiology on this is not clear).

The final chapter from Martin Williams (Defra) provides a historical perspective on UK air-quality policy development over the last 50 years. He discusses the role of the policy-maker in interpreting the science and in determining acceptable risk, evaluates the effectiveness of national instruments, hints at the limitations of the current system of air quality management based on achieving objective concentrations and advocates combination with the exposure-reduction approach to more equitably and cost-effectively protect public health, challenging air quality managers and policy-makers to 'think creatively' to achieve this goal. Finally, Williams examines the synergistic opportunities for tackling air quality and climate change as the focus for strategic urban policy development in the near future.

As a very broad overview of a complex subject, I would concur with the editors' recommendation of this book to air-quality practitioners in central and local government, consultancies and industry, environmentalists, policy-makers and students of environmental science, engineering and management courses. The book could equally inform interested non-experts, arguably the most valuable target audience to initiate changes necessary for improvements in air quality.

Caveat: the views presented here are those of the author and do not necessarily represent those of the University of the West of England.

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The ECG interview: Reclaiming the land

In the third ECG *Bulletin* interview, ECG committee member **James Lymer** describes his interests in improving the environment through his work on contaminated land risk assessment and amelioration.

What inspired you to become a scientist?

At school I didn't have a specific academic interest, although mathematics was a strong skill. It wasn't until I was 13 that my school taught separate science subjects of chemistry, biology and physics and this is when I developed a strong interest and aptitude for chemistry. My chemistry teacher at school and my tutor at college had both worked in the chemical industry as well as in education, and I decided to follow their recommendation to study a BSc (Hons) in Chemistry at the University of Bradford with a view to working in the chemical industry.

How did you come to specialise in Contaminated Land Risk Assessment?

Following on from my degree, I intended to pursue a career in synthetic organic chemistry and so I started postgraduate research at the University of St Andrews, where I was mostly working in the laboratory generating iminyl radicals and studying their cyclisations in order to prepare nitrogen heterocycles. Although I enjoyed problem-solving, understanding reaction mechanisms and structure elucidation, I decided that I wouldn't enjoy a long-term laboratory-based career and so I wrote up my research for an MPhil degree after one year.

After a spell of working in the voluntary sector (including a local environmental charity), I was recruited by a small environmental consultancy to apply my chemistry and analytical skills to help develop the expertise in chemical risk assessment (particularly contaminated land). This was a big change from synthetic organic chemistry as the work was multidisciplinary and I was working with colleagues from the fields of geology, hydrology and geotechnical engineering. After around eighteen months, I moved to my current employers, a national medium-sized engineering and

"… the earth seems to me a sterile promontory; … the air … a foul and pestilent congregation of vapours …"
Hamlet, act 2, sc. 2

environmental consultancy, Wardell Armstrong LLP.

Describe your work at the Facility for Wardell Armstrong LLP?

I work as part of the contaminated-land team at the Sheffield office, and we work primarily for private sector clients who are often seeking planning permission for the redevelopment of brownfield land.

My main role involves advising colleagues on the transport and fate of contaminants in soil and groundwater, assessing the risk to long-term human health and groundwater and agreeing remedial strategies with the Regulatory Authorities. Other aspects of my role involve classifying soil as waste in accordance with waste legislation, and on-site supervision of remedial works. For example, if the chemical concentrations of certain contaminants are significantly elevated so that they pose a substantial risk to long-term human health, then remediation such as contaminant source removal or treatment (chemical/physical/biological) will be required to reduce the risk to human health.

Working as one of various technical specialists, including geologists, engineers and environmental scientists is interesting, as you learn aspects of other technical areas and they can pick up information from you; this is one of the aspects of the job I enjoy the most. Another aspect I really enjoy is working outdoors, in particular carrying out what is called a “site visit walkover” which involves a non-intrusive inspection of a plot of land which could be a disused former tar works or a factory and “detecting” any potential sources of contamination. (See p 18, ECG *Bulletin*, July 2008).

What advice would you give to people considering a career in environmental chemistry?

If you enjoy applying your chemistry knowledge to multidisciplinary problems and would like to work outdoors for part of your working week, then I would recommend working in contaminated land for a career. Although remuneration may not be as high as other professions, there is variety in the job which I think is a big advantage. For example, you could be working on a site anywhere in the UK (World?) and then moving onto another site somewhere completely different with a different contamination problem to assess and solve.

What are some challenges facing the environmental chemistry community now?

From my experience there is a need for increased funding for UK-based scientific research in remediation techniques, primary science used in risk-assessment models (vapour migration) and in our understanding of factors affecting degradation reactions of organic chemicals in soil and groundwater. This would aid assessors in better understanding contamination issues at different sites and providing better remediation solutions.

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

Being part of the CLAIRE/EIC/AGS project to derive generic assessment criteria for human health. This involved working with other risk assessors from various environmental consultancies in collating and reviewing chemical and toxicology data for organic and inorganic contaminants and generating generic assessment criteria for human health. [This project is described on p. 36 of this issue].

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

Probably a historian, as I am particularly interested in the industrial revolution, but the scientific area is definitely my preferred choice of employment.

And what do you do when you are not working?

Outdoor pursuits (hill walking), “real ale connoisseur” and visiting places of historical interest or natural beauty.

Meeting Report

RSC General Assembly 2009

The RSC General Assembly functions as an advisory body to Council. Its role is to advise on the strategy, policy and activities of the RSC, enabling the views of members to be represented, and to facilitate communication and coherence within governance and the chemical science community. The RSC General Assembly comprises Council Members and representatives of the Local Sections and the Interest Groups. Representatives of some committees and other groupings may also be involved.

The fifth RSC General Assembly was held at the Birmingham Hilton Metropole Hotel from Friday, November 20th to Saturday, November 21st 2009, and some 180 delegates attended.

The meeting commenced with three plenary lectures. The first from **Sir John Banham** (Johnson Matthey plc) entitled "Chemistry in an era of austerity: an industrial perspective" surveyed the future landscape of the chemical industry. Innovation, research and high-value added intellectual skills are the future for chemistry in the UK, and Sir John emphasised how pressing the competition from developing nations has become over the last decade. There is a strong case for UK government investment in high-level education and in chemistry research, and this message was well received by delegates.

In his lecture, **Professor Jeremy Sanders** (University of Cambridge) discussed "The national and international challenge for chemistry". Modern chemistry features in a range of new and emerging disciplines: cell biology, materials science, proteomics, genetics were all mentioned. What was salient was the centrality of chemical knowledge and experience to the advancement of all of these endeavours. Chemists and chemistry are a crucial element of the multidisciplinary research teams needed to develop and exploit these challenges.

The third plenary lecturer, **Antony Williams** (ChemSpider, RSC) spoke on "Connecting chemists to the Internet through *ChemSpider*" and the problems with uncurated databases of chemicals, and he gave some examples of issues of nomenclature and structure which ChemSpider will systematically tackle (see: www.chemspider.com/blog and www.slideshare.net/AntonyWilliams).

Friday afternoon gave the delegates an opportunity to participate in two Discussion Sessions (from a selection of eight). I first attended a session on "Working together at a local level" which brought together local groups. Most of the comments concerned the large number of 'sleeper' members in the RSC, which produces difficulties in generating interest in the RSC Section activities and committees. This is compounded by the way both industry and academia have reduced the encouragement they give to employees to attend and participate in RSC activities.

The second session I attended considered the EPSRC *2009 International Review of UK Chemistry Research* (available *via* the RSC web site). The review concluded that UK chemistry was in a healthy state. Industry-academic links had grown and research was of a high internationally recognised standard. There was a problem with support for early career researchers (ECRs), which meant that adventurous research was not encouraged. Questions were raised at this session about the review:

- Was it too anodyne in its identification of the challenges for the future?
- Did it lack specificity in offering direction to government policy for chemistry?
- Did it reflect the real concerns about the abilities of the products of the research schools?
- Did it tackle the need for ongoing investment in the continuous updating and maintenance of the equipment base in UK chemistry

The RSC response is to seek ways to encourage ECRs, develop regional strengths, consider the nature and status of PhD training, and improve communications with the Research Councils.

The evening dinner and prize ceremony gave awards and prizes to some twenty-five members of the RSC. The Environment Prize (sponsored by Procter and Gamble) was awarded for outstanding contributions to the chemical sciences in the area of environment, sustainability and energy. The 2009 winner was Professor James Durrant (Imperial College). Professor Durant is Deputy Director of Imperial College's Energy Future Laboratory and his research interests are focused on solar energy conversion by nanostructured and molecular materials – harnessing solar energy either to produce electricity (photovoltaics) or molecular fuels (such as hydrogen). Currently his group (which works closely with several industrial partners) is working on both polymer/fullerene and dye-sensitised nanocrystalline solar cells and photoelectrodes for water photolysis, as well as a spin-off application in heterogeneous sensing of pollutants.

On the Saturday morning, I attended the Annual Meeting of RSC Interest Groups, which went through a previously circulated sixteen-point agenda. Of interest here is the fact the ECG is the largest interest group with 1200 members (slightly down from 1225 in 2008). Representatives from the RSC's Historical Group and the Physical Organic Chemistry Group gave presentations. There was discussion on MyRSC Online Community (http://my.rsc.org/home) and plans for encouraging its use and growth. The RSC Roadmap (http://www.rsc.org/roadmap), and the introduction of an all-inclusive membership subscription in 2011 (see below) were also considered by the delegates.

Dr LEO SALTER,

December 2009

Royal Society of Chemistry Interest Groups

RSC Interest Groups (Divisions, Forums and Groups) play an important role in contributing to the many RSC activities in support of the chemical sciences. From 2011, the arrangements for RSC members for joining RSC Interest Groups, such as the Environmental Chemistry Group, will change.

The introduction of an all-inclusive membership subscription in 2011

At the Annual RSC Interest Groups meeting in 2008, held at the General Assembly, members were informed that the proposal for an all-inclusive membership subscription was being considered by Council. This followed on from discussions with Interest Groups during the previous 12 months.

The final proposal was agreed by Council in March 2009 and will be introduced in 2011 enabling all members to join up to three Interest Groups as part of the annual RSC membership subscription. Membership of any additional groups will be charged at **£10 per group**.

In 2011, all Groups will receive a block grant equal to the subscription income received in 2010, plus an additional transition payment. The RSC will ensure that no group is financially disadvantaged by the introduction of the new subscription structure. An initial estimate of 2010 income will be provided to all groups in July.

In advance of transition to the all-inclusive subscription, Council also agreed that a minimum level of £5 should be applied to all Group subscription rates in 2010.

RSC Interest Groups: http://www.rsc.org/Membership/Networking/InterestGroups/index.asp

RSC Group Handbook: http://www.rsc.org/InterestGroupHandbook

In summary:

- The all-inclusive membership fees will take effect with the 2011 subscription.
- RSC membership will include membership of up to three Interest Groups.
- Membership of each additional Group will cost members £10.
- Each Group will receive a block grant equal to their 2010 income and a transition payment for 2011 of £100.
- From 2012 Groups will receive a block grant plus a *per capita* payment of £1 per member above the 2010 figure. The block grants will be reviewed after the first three years.
- If an individual Group experiences a large increase in numbers during this transition period, the RSC will deal with this on a "case by case" basis.

Exposure to contaminated land and human health: a CL:AIRE report

CL:AIRE [Contaminated Land: Applications in Real Environments] is an independent, not-for-profit organisation which has been established to stimulate the regeneration of contaminated land in the UK by the application of practical sustainable remediation technologies. In December 2009, CL:AIRE published a report – *The Soil Generic Assessment Criteria for Human Health Risk Assessment* – which is intended as an aid in the assessment of risk to human health from exposure to contaminated land.

In order to attempt to quantify the concentration of a contaminant that may represent a risk to human health, there is a need to understand the toxicological and physico-chemical properties of the substance. These properties can then be used within a mathematical model to estimate exposure to receptors and the likely significance of the exposure with respect to human health.

To help assessors in determining whether the degree of contamination at a site is a risk to human health, the Environment Agency (EA) has developed an updated version of the Contaminated Land Exposure Assessment (CLEA) model and background guidance. The EA has also published a compilation of physico-chemical data for priority organic pollutants (SR7) and toxicology reports on specific contaminant, which allow the CLEA model to be used to create Generic Assessment Criteria (GAC). GAC derived by the EA, and published after a review by various government departments, are called Soil Guideline Values (SGV), which, when applied correctly, represent a level below which there is considered to be a minimal risk to human health from long-term exposure to the soil.

The use of SGV as screening values is extremely useful in initial assessments of potentially contaminated sites, and can help to screen out individual contaminants or even entire sites from more complex detailed quantitative risk assessment. However, historically, the EA has been slow to produce SGV and the baseline data on toxicological and physico-chemical parameters. These data are required in order to use the CLEA model to produce GAC or more site specific assessment criteria (SSAC). In the past this has led to many organisations deriving their own database of input parameters and GAC values resulting in a myriad of values and duplicated effort across organisations.

In late 2008, members of the Environmental Industries Commission (EIC) Contaminated Land Working Group agreed to collaborate to help fill this gap by producing a set of industry-agreed input parameters and GAC values for as many substances as possible. Member organisations were asked to provide professional staff with experience in risk assessment of contaminated land, and the AGS (Association of Geochemical & Geoenvironmental Specialists) and CL:AIRE also joined the project. Forty-seven professionals from twenty-six companies collaborated.

Toxicological and physico-chemical data on 44 contaminants were compiled and assessed. GAC for four standard generic land uses (residential with and without consumption of home-grown produce, allotments and commercial) and three soil organic matter contents (1%, 2.5% and 6%) were then computed for 35 of these substances using the CLEA (v1.06) model..

The final report is the culmination of hundreds of hours of work by experts from the twenty-six companies, and is available for free from the CL:AIRE website (http://www.claire.co.uk/). An Excel spreadsheet containing all of the input parameters required for the CLEA (v1.06) model can also be downloaded.

It is hoped that the GAC values and input parameters produced by this study will be used by all involved in the assessment of contaminated land. The best reward for all those who worked on the project will be for the contaminated land community to regularly use the GAC values for the assessment of risk to human health from exposure to contaminated land.

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December 2009

Meeting report: Royal Society of Chemistry Environmental Chemistry Group

Atmospheric Chemistry Forum

The ECG organised an ***Atmospheric Chemistry Forum*** at Burlington House, London in April 2009 for PhD students and early career post-doctoral researchers. The aims of the meeting were:

- to provide a forum for delegates to discuss current research topics;
- to present their work to their peers, either as a 15 minute talk or as a poster presentation; and
- to exchange expertise and foster links between individual members of research groups.

Following the success of this inaugural meeting, a second ***Atmospheric Chemistry Forum*** is being planned for 2010/2011. RSC Travel Grants will again be available for suitable applicants.

A selection of abstracts from the 2009 ***Atmospheric Chemistry Forum*** is presented below.

1 Exploring the Formation of Cold Ice Clouds

Theodore W. Wilson[1], Benjamin J. Murray[1], Ottmar Möhler[2] and Steven Dobbie[3]

1: School of Chemistry, University of Leeds 2: Institute for Meteorology and Climate Research, Forschungszentrum Karlsruhe 3: School of Earth and Environment, University of Leeds

Recent studies[1,2] have shown that solution droplets containing surrogates of atmospheric oxygenated organic material can transform into ultra viscous or glassy (amorphous solid) particles at temperatures relevant to the Tropical Tropopause Layer (TTL). Here we present experiments which were performed at the AIDA (Aerosol Interaction and Dynamics in the Atmosphere) atmospheric simulation chamber using citric acid (a surrogate for the oxygenated organic material found in the atmosphere) solution aerosol. It was found that at temperatures above the glass transition, ice was formed at the homogeneous freezing threshold (**Figure 1**, runs 1 and 4) as would be expected. At temperatures below the glass transition (i.e. aerosol was in a glassy state), ice was formed at relative humidities below the homogeneous freezing threshold (**Figure 1**, runs 2, 3 and 5). This indicates that glassy aerosol heterogeneously nucleates ice which has important implications for our understanding of cirrus cloud formation in the TTL. A 1D cirrus model is currently being used along with parameterisations of data collected at AIDA to assess the impact of heterogeneous nucleation by glassy

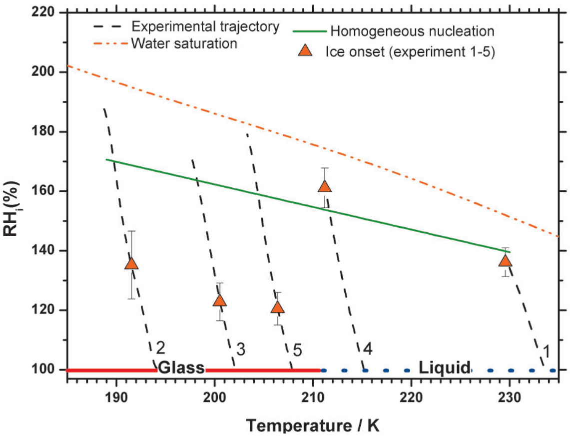

Figure 1 *[Wilson et al.]. Experimental RH_i (relative humidity with respect to ice) and temperature trajectories (black dashed lines) with associated ice formation onsets (orange triangles). Ice formation was detected by laser depolarisation measurements. Experiments were performed using the same citric acid solution aerosol, which was introduced initially at 234 K. Numbers 1 -5 represent the order in which experimental runs took place. The orange dash-dot-dot line represents the water saturation line. The green solid line is the expected onset of homogeneous freezing for liquid solution aerosol and is parameterized from data collected*

aerosol on in-cloud saturation and ice particle number.

1 B. J. Murray, Inhibition of ice crystallisation in highly viscous aqueous organic acid droplets, *Atmos. Chem. Phys.*, 2008, **8**, 5423-5433.
2 B. Zobrist, C. Marcolli, D. A. Pedernera and T. Koop, Do atmospheric aerosols form glasses?, *Atmos. Chem. Phys.*, 2008, **8**, 5221-5244.
3 Möhler, O. *et al*., , Atmos. Chem. Phys., 2003, **3**, 211–223.

2 Kinetic and Thermochemical Studies of the ClO + ClO + M D $\rightleftarrows$ Cl_2O_2 + M reaction

Valerio Ferracci and David M. Rowley

Department of Chemistry, University College London

A recent paper by von Hobe *et al.*[1] highlighted significant inconsistencies between laboratory results, theoretical calculations and field observations concerning the ClO dimer cycle, one of the most effective ozone-depleting catalytic cycles operating in the Antarctic winter. This work has investigated the temperature dependence of one of the key reactions in this cycle, ClO + ClO + M D $\leftrightarrows$ Cl_2O_2 + M (1, −1). ClO radicals were generated *via* laser photolysis of Cl_2/Cl_2O/air mixtures and their concentration was monitored *via* UV absorption spectroscopy. The use of a Charge Coupled Device (CCD) detector allowed time resolution over a broad spectral range. The equilibrium constant K_{eq} was determined as the ratio of the rate constants of reactions (1, −1) over the T range 256–312 K. The standard enthalpy and entropy changes of reaction 1, $\Delta_r H°$ and $\Delta_r S°$, were determined form the measured equilibrium constants *via* Second Law and Third Law analyses. The values obtained from the Second Law analysis ($\Delta_r H°= −80.8 \pm 2.2$ kJ mol$^{−1}$; $\Delta_r S°= −168.4 \pm 7.9$ J K^{-1} mol$^{−1}$) are greater in magnitude than current NASA recommendations, implying a different partitioning between ClO and Cl_2O_2, shifting towards the dimer.

1 M. von Hobe, M., R. J. Salawitch, T. Canty, H. Keller-Rudek, G. K. Moortgat, J.-U. Grooß, R. Müller and F. Stroh*,* Understanding the kinetics of the ClO dimer cycle, *Atmos. Chem. Phys. 7, 3055,* 2007**.**

3 Large floral emissions of estragole from oil palm plantations can impact atmospheric chemistry

Pawel K Misztal[1,2], Mathew R Heal[2], J Neil Cape[1] and other authors (see ref 2)

1: Centre for Ecology & Hydrology 2: School of Chemistry, University of Edinburgh

Estragole (methylchavicol; IUPAC name:1-allyl-4-methoxybenzene) is a known attractant of the African oil palm weevil (*Elaeidobius kamerunicus*), which pollinates oil palms (*Elaeis guineensis*). The same compound is also commercially available as an insecticide (*e.g.* against the bark beetle). There has been recent interest in the biogenic emissions of estragole[1] but it is normally not included in atmospheric models of biogenic emissions and atmospheric chemistry. Recently, we reported the first direct canopy-scale measurements of estragole fluxes from tropical oil palms by the virtual disjunct eddy covariance technique[2]. The observed ecosystem mean fluxes and mean ambient volume mixing ratios (**Figure 2**) of estragole are the highest reported so far (0.49 mg m^{-2} h^{-1} and 3 ppbv respectively). Although a C-10 compound, estragole is not regarded as a monoterpene. However, its SOA mass yield from photochemical oxidation was reported at 40% which was in a similar range or higher than that of oxygenated terpenes.[3] With more than 14 million ha of plantations globally (more than 60% in Malaysia and Indonesia),[4] this may have an impact on atmospheric chemistry that previously has not been accounted for in models and could become more important in the future due to expanding oil palm plantations.

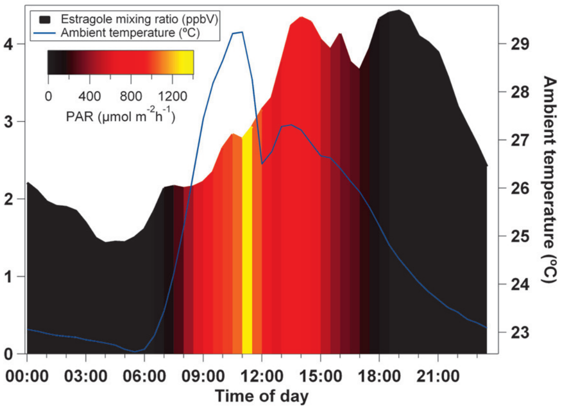

Figure 2 *[Misztal et al.]. Average diurnal cycles of estragole mixing ratios (upper boundary of shaded area; left axis) in relation to temperature (in blue; right axis) and PAR (colour scale).*

1 Bouvier-Brown, N. C. *et al*., Methyl chavicol: characterization of its biogenic emission rate, abundance, and oxidation products in the atmosphere, *Atmos. Chem. Phys*., 9, 2061-2074, 2009.
2 Misztal, P. K., Owen, S., Guenther, A., Rasmussen, C., Geron, C., Harley, P., Phillips, G., Ryan, A., Edwards, D. P., Hewitt, C. N., Nemitz, E., Siong, J., Heal, M. R., and Cape, J. N.: Large estragole fluxes from oil palms in Borneo, *Atmos. Chem. Phys. Discuss.*,submitted, 2009.
3 Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.-Atmos.*, 111, 10.1029/2006jd007050, 2006.
4 FAOSTAT Online Statistical Service. Item: Oil palm fruit; element: area harvested; year: 2007; country: World, South East Asia, Malaysia, Indonesia. http://faostat.fao.org, 2009.

4 Characterising the Optical Properties of Aerosol Particles by Cavity Ringdown Spectroscopy

Rachael E.H. Miles, Svemir Rudić, Andrew J. Orr-Ewing and Jonathan P. Reid

School of Chemistry, University of Bristol

Atmospheric aerosol can be liquid or solid in phase, with particles either directly emitted into the atmosphere from natural and anthropogenic sources, or formed *in situ* from gas-to-particle conversion processes. The radiative forcing effect of aerosol is characterised by its optical properties, which are dependent on particle size, shape, composition, mixing state, phase and illumination wavelength. The direct interaction of aerosol with atmospheric radiation through scattering and absorption leads to an overall global negative climate forcing. However, the current level of scientific understanding in this area is classified as low[1], with the temporal and spatial variability of aerosol, coupled with the wide range of chemical compositions and particle morphologies found in the atmosphere, making it a challenging field of study.

We present the benchmarking of a new aerosol cavity ringdown (A-CRDS) instrument to measure the optical properties of accumulation mode aerosol as a function of particle composition, size and illumination wavelength. This represents the first use of A-CRDS to characterise the change in aerosol optical properties over a narrow wavelength range of a few tens of nanometres. Sub-micron diameter polystyrene beads were used as analogues for a spherical, purely scattering aerosol system.

1. S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Averyt, M. Tignor and H. L. Miller, eds. IPCC, 2007: Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, United Kingdom and New York, USA: Cambridge University Press.

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5 Ultra-sensitive spectroscopy of optically-tweezed aerosol droplets: absorption and fluorescence

Kerry J. Knox, Caroline H. Berry, Laura Mitchem and Jonathan P. Reid

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The effect of aerosols represents the largest uncertainty in the current knowledge of anthropogenic radiative forcing; the understanding of the effects of aerosols must be furthered if we are to accurately predict future climate change[1]. Absorption of light by aerosol particles is a process that is central to understanding the effects of aerosols in the atmosphere[2]. A new technique for measuring the optical absorbance of a single aerosol droplet has been developed, capable of measuring absorbances of less than 2×10^{-7} over an optical pathlength of less than 10 μm[3]. The technique uses a combination of aerosol optical tweezers and cavity-enhanced Raman spectroscopy[4]. This approach represents a highly promising technique for probing the absorption of weakly-absorbing particles, with the capability to detect temperature changes as low as a few milli-Kelvins.

By introducing fluorescent chromophores to the droplets, cavity-enhanced fluorescence and a four-wave mixing process have been observed for optically-tweezed aerosol droplets for the first time (**Figure 3**). Making use of the four-wave mixing process, the quality factor of an optically-tweezed aerosol droplet as an optical cavity has been quantified. This represents a significant step towards investigating the absorption behaviour of more strongly absorbing liquid particles.

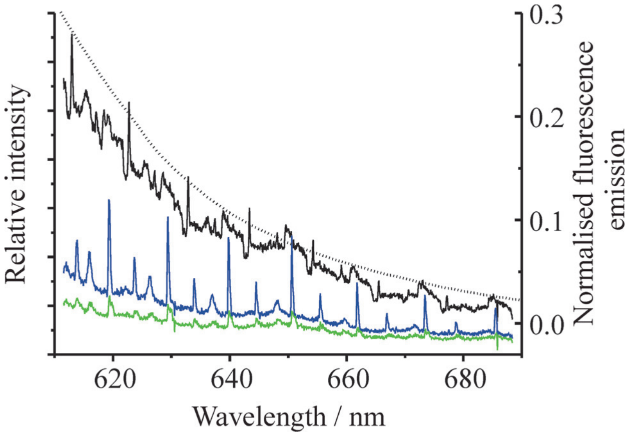

Figure 3 *[Knox et al.] Cavity-enhanced fluorescence spectra collected from an optically-tweezed aqueous droplet containing Rhodamine 6G. The spectra were recorded at 1 second intervals, in order from earliest to latest shown in black, blue and green, respectively. The fluorescence intensity decreases with time as a result of photobleaching. A dotted line shows the normalised fluorescence emission from a bulk sample of Rhodamine 6G.*

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4. L. Mitchem and J. P. Reid, Optical manipulation and characterisation of aerosol particles using a single-beam gradient force optical trap, *Chem. Soc. Rev.*, 2008, 37, 756

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6 Street Canyon Atmospheric Composition: Coupling Dynamics and Chemistry

Vivien Bright, William Bloss and Xiaoming Cai

School of Geography, Earth & Environmental Sciences, University of Birmingham

Atmospheric composition within the urban environment, particularly within street canyons (formed by a road running between two rows of buildings) has a direct effect on the air quality of an environment in which a large majority of people live and work. The composition of air within the urban canopy is determined by the composition of background air that is mixed in from above the canyon, vehicle exhaust and other emissions from within the street, together with the mixing and chemical processing of pollutants within the canyon.

This study aims to build upon an existing dynamical model of atmospheric motion (Large Eddy Simulation (LES) model) within the canyon by adding a more detailed chemical reaction scheme. The enhanced model will then provide a unique tool to further investigate the combined effects of mixing and chemical processing upon air quality within the street canyon. Initially, a zero-dimensional box model will be used to investigate chemical changes and a number of 'emission scenarios' that could be applied to the LES. Subsequently, a suitable "reduced" chemical scheme to include within the LES will be evaluated using the box model. The reduced chemical scheme will then be incorporated into the LES to be used in further investigation.

7 Long-term monitoring of Volatile Organic Compounds (VOCs) in the free troposphere above the UK

Shalini Punjabi, James R .Hopkins, Alastair C. Lewis

Department of Chemistry, University of York

Initial results are presented from a long-term study of Volatile Organic Compounds (VOCs) in the free troposphere. VOCs influence not only local, regional and global photochemistry but also have a strong indirect influence on climate through ozone and methane oxidation cycles. Short-term studies provide information about the state of the atmosphere at a specified time and location, but in order to study seasonal and inter-annual variability in the atmosphere, long term monitoring is required. The study is conducted during UK flights aboard the FAAM BAe146 aircraft. Samples are collected using the Whole Air Sampling (WAS) system and subsequently analysed using a dual channel gas chromatograph with flame ionization detector. An important aspect of this study is the regular calibration of the instrument using a certified mixture of trace gases to obtain an accurate and reliable VOC measurement. The analysis method and calibration will be discussed in detail. The VOC data will be evaluated in conjunction with other chemical and meteorological parameters measured aboard the aircraft to understand the factors that control their distribution.

8 Characterisation Of Urban Particulate Matter In The UK

M.D. Hammonds, M.R. Heal

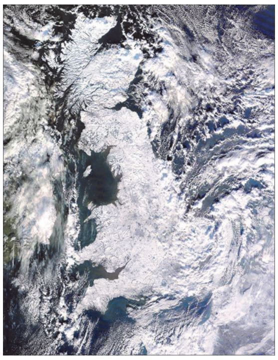
School of Chemistry, University of Edinburgh

The aim of the PhD project is to contribute understanding both to the exact nature and origin of some of the carbonaceous fraction of particulate matter (PM).

Samples of PM_{10} (particles with a diameter smaller than 10 μm) are eing collected from an urban background location in Edinburgh (St Leonards; OS Grid Reference: NT263731) using a Partisol 2025 sampler. This locality provides PM that is more representative of suburban background air compared to a roadside site, which will be more directly influenced by traffic-related emissions. PM concentration (μg m-3) and the level of black smoke (BS) have been determined for each daily filter sample.

The next objective is to undertake multi-stage analyses of the water soluble and insoluble OC using various techniques, in order to characterise, in a much more detailed manner, chemical aspects of this complex component of airborne PM. Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) have been used to analyse standard PM reference materials obtained from the National Institute of Standards and Technology (NIST).

Abstracts edited by Bill Bloss & Stephen Ball



UK's sub-zero terrestrial and lower atmospheric environments, 7th January 2010 [NASA's Terra satellite image]

News from the RSC Library and Information Centre

RSC Library. The refurbished RSC Library opened in October 2009 and now forms part of the RSC's Chemistry Centre. The Centre is a suite of rooms within the RSC's Burlington House offices that can be used by the RSC, members and external organisations to host a range of events, from committee meetings and seminars to report launches and public lectures.

The Chemistry Centre is made up of six rooms in total. On the first floor of the building are the interconnecting rooms of the Library, Coffee Area, Council Room, and Hinshelwood Room, along with the adjacent Priestley Room (see plan). The Fish Room on the ground floor completes the venue.

For RSC members who are visiting London, the Chemistry Centre offers a variety of facilities:

- The **Members' Office** (formerly part of the old East Gallery) is a quiet space next to the Library equipped with computers and with access to *Chemical Abstracts* on CD-ROM (10th-15th CI periods); ACS and RSC online journals; and the RSC Virtual Library.
- A **coffee area** (formerly the RSC Librarians' Office at the entrance to the main Library) where free tea and coffee and newspapers are available throughout the day, and with wireless internet access for laptop users.
- The main **Library** area (containing much of the RSC's collection of printed journals and books), which can be visited at select times throughout the week for research.

However, because these facilities may be in use for RSC functions, externally-organised meetings, *etc.*, it is necessary to check online *via* the RSC Library and Information Centre (LIC) web pages to confirm their availability before visiting the Chemistry Centre.

The RSC Library at Burlington House

The RSC Virtual Library. The RSC Library supports members' information needs wherever they are 24/7 through the RSC Virtual Library and the Chemistry Search Service. Topics covered by recent enquiries from members include:

- detection of biotoxins in shellfish
- REACH Legislation
- fermentation for biofuels.

Examples of some recently acquired full-text e-books on the environment, health and safety, and toxicology for the RSC Virtual Library include:

Knovel

- *Air Pollution and Health*
- *Guidelines for Chemical Transportation Safety, Security, and Risk Management*
- *Nanotechnology: Toxicological Issues and Environmental Safety*

Referex

- *Critical Temperatures for the Thermal Explosion of Chemicals: Industrial Safety Series*
- *Still Going Wrong!: Case Histories of Process Plant Disasters*

and How They Could Have Been Avoided
- *Loss Prevention and Safety Promotion in the Process Industries*

Net Library

- *Riot Control Agents: Issues in Toxicology, Safety, and Health*
- *Globally Harmonized System of Classification and Labelling of Chemicals*
- *Nanotechnology: Environmental Implications and Solutions*

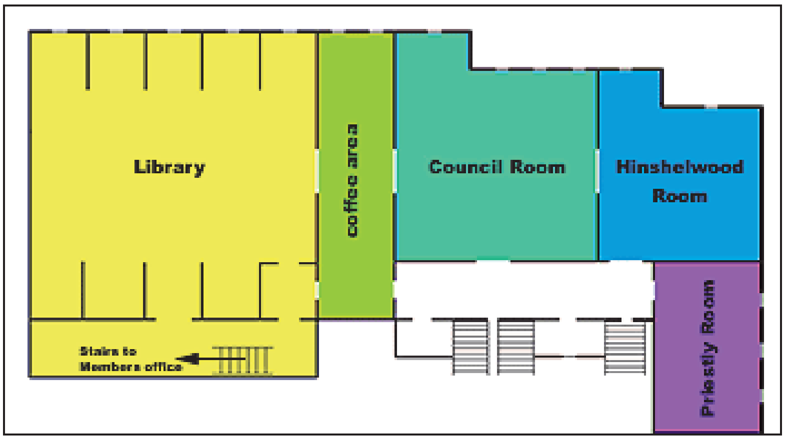
And some full-text e-journals, which are available through the Virtual Library:

- *Energy & Environment*
- *Environment*
- *Journal of Environmental Health*

Recent acquisitions of printed books. The RSC Library is no longer actively extending its collection of printed chemistry books. A few key reference and other books will continue to be bought, and new books published by the Royal Society of Chemistry, Cambridge will be added to the collection along with any donations to the Library. The following titles on the environment, health and safety, and toxicology have been acquired since June 2008:

Bretherick's Handbook of Reactive Chemical Hazards, 7th Edition: Volumes 1 & 2

P. G. Urben, (ed.), Elsevier, Oxford, UK, 2007; Shelf Mark: 614.8 R



Plan of the Chemistry Centre

Calculated Risks: The Toxicity and Human Health Risks of Chemicals in our Environment

J. V. Rodricks, Cambridge University Press, Cambridge, UK, 2007; Shelf Mark: 628.52

The Food Safety Hazard Guidebook

R. Lawley, Royal Society of Chemistry, Cambridge, 2008; Shelf Mark: 664:614.8

There is a Library & Information Centre Group on the online community site MyRSC for discussions on anything relating to chemical information. Views and comments about the services provided by the LIC are welcome. Registration to MyRSC is free. Stay in touch with developments and news of the LIC at Library@rsc.org

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Forthcoming Symposium

Geochemical Speciation & Bioavailability of Trace Elements: Progress, Challenges & Future Trends

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Date: 7 — 8th September 2010

Venue: Lancaster University, UK.

Sponsors: Environmental Mineralogy Group and the RSC Environmental Chemistry Group

Elemental speciation analysis is increasingly recognised as key to understanding the behaviour of pollutants in aquatic and terrestrial environments. Models that are able to predict elemental reactivity, bioavailability and transport are needed to better assess short and long-term risks from trace elements in the environment. As yet, geochemical models are limited in the extent to which they incorporate the formation kinetics and transport properties of metal and radionuclide complexes, and colloidal associations, in a fully mechanistic way.

This two- day conference aims to bring together geochemists, aquatic chemists, mineralogists, biologists, toxicologists and engineers to discuss recent progress in this field and identify avenues for future research and collaboration. Thus, it gives us great pleasure to invite scientists, technologists, students, legislators, government officials, and all those who are interested in studying and predicting the speciation and bioavailability of key trace elements in the environment to participate in this conference.

The conference comprises plenary poster sessions and nine keynote lectures by experts in the field :

(1) Dr. **Jon Petter** Gustafsson (Royal Institute of Technology, Sweden)
(2) Prof. **Erik Smolders** (Leuven University, Belgium)
(3) Dr. **Dmitrii Kulik** (Paul Scherrer Institute, Switzerland)
(4) Prof. **Willem Van Riemsdijk** (Wageningen University, Netherlands)
(5) Prof. **Herman Van Leeuwen** (Wageningen University)
(6) Dr. **Scott Young** (Nottingham University)
(7) Prof. **Stan Van den Berg** (Liverpool University)
(8) Dr. **Hao Zhang** (Lancaster University)
(9) Dr. **Steve Lofts** (Centre of Ecology and Hydrology, Lancaster).

Registration & payment:

Participation is ***limited to 70 delegates*** owing to space restrictions, thus pre-registration is encouraged. Registration will be £90 per person (if paid by 30th April 2010, £110 thereafter) with a student rate of £55 per person (before 30th April 2010, £75 thereafter). Registration includes refreshments, lunches, conference dinner, car parking, book of abstracts, *etc.* B&B accommodation will be at the University campus, with en suite rooms at £46 per night. *Deadline for abstract submission for poster presentations is 30th July 2010*. Abstracts should be emailed to I.ahmed@lancaster.ac.u.

Registration and further information can be found at

http://minersoc-emg.org/events/GeoSpec2010.html

The Environmental Mineralogy Group (EMG) is a Special Interest Group of the Mineralogical Society of Great Britain and Ireland.

Contact Details

Conference Organisers: Dr Imad Ahmed (Lancaster University; email: I.ahmed@lancaster.ac.u) & Dr. Elizabeth Bailey (Nottingham University; email: liz.bailey@nottingham.ac.uk).

The ECG *Bulletin* is printed on paper made from wood pulp sourced from sustainable forests, and is suitable for archival storage. This issue of the ECG *Bulletin* was printed by Sureprint, 1 Eastern Road, Haywards Heath, West Sussex RH16 3NG Tel: 01444 456673.

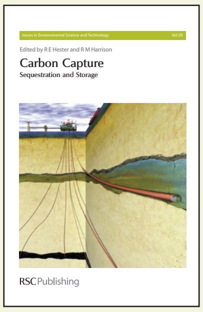
Issues in Environmental Science and Technology

Series Editors

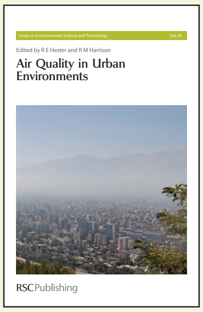
R E Hester, University of York, UK | **R M Harrison,** University of Birmingham, UK

This comprehensive series from RSC Publishing has been devised to tackle important environmental topics in response to the rapid growth of interest in this area and the need for authoritative reviews of such topics. Issue are published twice a year with each volume addressing a specific topic.

Written by world experts in their specialised fields, the series presents a multidisciplinary approach to pollution and environmental science and, in addition to covering the chemistry of environmental processes, focuses on broader issues; notably economic, legal and political considerations.



Title: Carbon Capture
ISBN: 9781847559173
Price: £54.95
Publication date: 22/12/2009
Description: Reports on methods of capturing and storing CO_2 from major sources to reduce the levels emitted to the atmosphere by human activities.

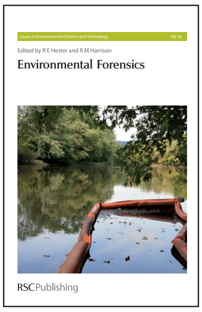


Title: Air Quality in Urban Environments
ISBN: 9781847559074
Price: £54.95
Publication date: 31/07/2009
Description: Provides comprehensive coverage of urban air pollution from sources through atmospheric processes, to human exposure and effects on health and the policy response.

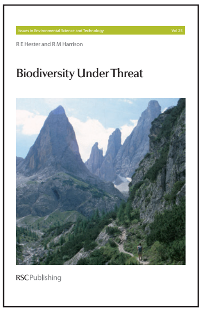
Title: Electronic Waste Management
ISBN: 9780854041121
Price: £49.95
Publication date: 03/12/2008
Description: This volume presents an up-to-date review of the scale of the electronic waste problem, the impact of recent legislation, current and future methods for treatment, recycling and disposal.

Ecosystem Services new for 2010!

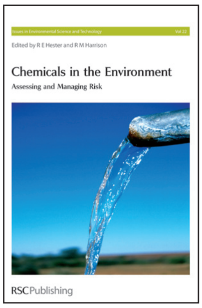
Other volumes available



"...this is a very useful book and gives an excellent position statement on the application of the techniques and of their limitations in environmental forensics." Reviewed in *Chemistry World.*



"The present book provides a very valuable introduction into environmental science and technology in general…" Reviewed in *Chemistry World.*



A bang up-to-date account of current and near-future legislation governing the assessment of risk and the management of chemicals in the environment. Reviewed in *ScienceDirect.*

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