



January 2008

Bulletin

RSC | Advancing the
Chemical Sciences

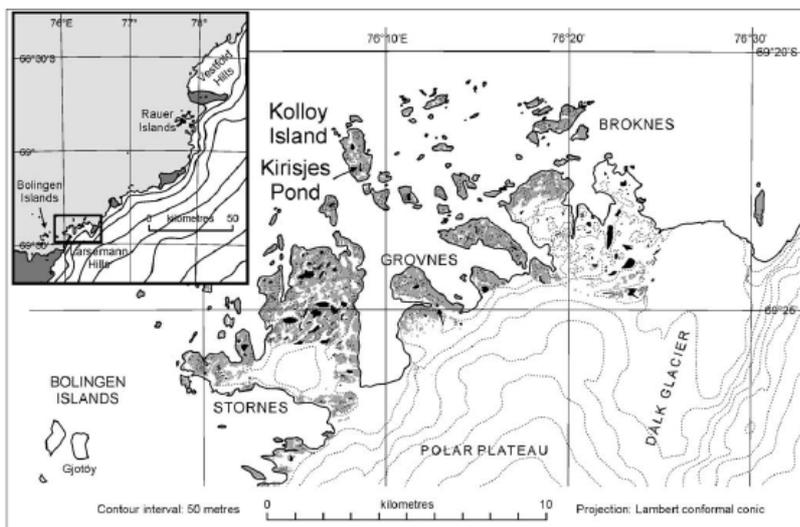
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Map showing the location of Kirisjes Pond in eastern Antarctica. Provided courtesy of the Australian Antarctic Division, Australian Antarctic Data Centre (<http://www-aadc.aad.gov.au/>) with modifications by Nick McWilliam, British Antarctic Survey. *Porphyrim analysis of sediment from Kirisjes Pond is a sensitive marker of past changes in the environment in this region: p. 2*

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News of the Environmental Chemistry Group

Chairman's report for 2007

Over the past year we have continued with the regular business of the group, producing the *ECG Bulletin*, maintaining the **ECG web pages**, and organising the **ECG Distinguished Guest Lecture**.

ECG web pages

We would welcome any suggestions for additional content on our web pages or for particularly useful web links to sources of environmental information.

Atmospheric chemistry representation

Last year, in response to an awareness of a lack of representation for the Atmospheric Chemistry community within the RSC's Interest Groups, we created a new position on the committee to consider the particular

needs of this group. There is a strong activity in atmospheric chemistry within the UK, and we felt that it was appropriate for the ECG to give specific consideration to their needs and to try to ensure that they consider the group as a natural home within the RSC.

ECG Distinguished Guest Lecture

The ECG Distinguished Guest Lecture and symposium in 2007 was organised for the first time as a full day event and as a result we were able to invite five speakers to take part. The ECG Distinguished Guest Lecturer for 2007 was Dr Eric Wolff from the British Antarctic Survey. The event was very successful and was well attended. We have decided to maintain this one-day format for the **2008 ECG Distinguished Guest Lecture**, which will take place on Wednesday 12th March 2008. The theme of the meeting will be "The Science of Carbon

Trading" and the meeting will cover the research behind the government policies and financial instruments that drive the carbon trading agenda. The **2008 Distinguished Guest Lecturer** will be the Director of the Cambridge Centre for Climate Change Mitigation Research, **Dr Terry Barker** (University of Cambridge).

ECG Committee vacancy

We have a vacancy on the ECG committee at the present time. If any ECG member would like to be considered for this place on the committee, please contact the Hon. Secretary of the ECG, Jo Barnes.

BRENDAN KEELY

Chairman, Environmental Chemistry Group,
December 2007

Sediment records of environmental change in Antarctica

Dr Brendan Keely from the University of York, and the current Chairman of the Environmental Chemistry Group, explains how the pattern of substitution of porphyrin pigment derivatives found in sediments extracted from Antarctic lakes is a sensitive marker of past climates and environmental change.

Introduction

Climate variability. In recent years, scientists, the public and policy makers have become keenly aware of the far-reaching consequences that climate change could have for society in the near future. Notably, parts of the Antarctic are already experiencing rapid warming events that have occurred at a greater rate than in other parts of the Earth [1].

Since the ice cover in the region represents over 70% of the world's freshwater, and some is close to the melting point, rising temperatures have the potential to cause the release of

considerable volumes of freshwater to the oceans. The consequent change in the balance of energy exchange between the ice, ocean and atmosphere would have significant impact on the world's climate. Records of past natural climate variability hold the key to understanding how temperature changes affecting Antarctica would influence other regions of the Earth.

Influence of the southern hemisphere on climate. The Quaternary (the last 1.7 million years) was marked by several glacial/interglacial events. Evidence suggests that the last two deglaciation events in the southern hemisphere triggered major changes in climate, including abrupt climate warming, in the northern hemisphere [2, 3].

The Holocene (the last 11,500 years) was marked by many, often rapid, temperature excursions that were of sufficient magnitude to affect human populations through drought, crop failure, floods and extreme weather events. In order to recover temporally detailed and well-resolved records of environmental change, such as changes in relative sea-level during the Holocene and beyond, it is necessary to

have highly sensitive and universally applicable methods that can be applied to sediments.

Lake sediments as records of environmental change. Sediments have the potential to record and store long-term records of environmental conditions. Lake sediments are particularly valuable since they often contain undisturbed records and the origins of the sediments are constrained by the lake morphology and location. Lake sediments contain organic residues originating from the various natural product compounds produced by the organisms that inhabited the water column at the time the sediment was deposited. Sedimentary organic compounds that show structural relationships to the natural product from which they originated can be used as **biological markers** to provide information on the composition of the biological community.

Accordingly, depth profiles of biological markers through cores of lake bottom sediments reveal changes in the populations of aquatic organisms over time. Such changes in population are driven mainly in response to changes in environmental conditions.

Chlorophyll pigments as biological markers

Derivatives of chlorophyll pigments are particularly useful biological markers [4]. Because they originate exclusively from the primary producer community, the pigments reflect the base of the food chain and hence the major groups of organisms that inhabited the lake waters at any point in time. Based on the nature of the tetrapyrrole macrocycle, several distinct types of chlorophyll pigment can be recognised in extant organisms, including pigments unique to eukaryotes (e.g. **chlorophylls a** and **b**; Figure 1) and others that exist only in photosynthetic bacteria (e.g. **bacteriochlorophylls c** and **d**; Figure 2).

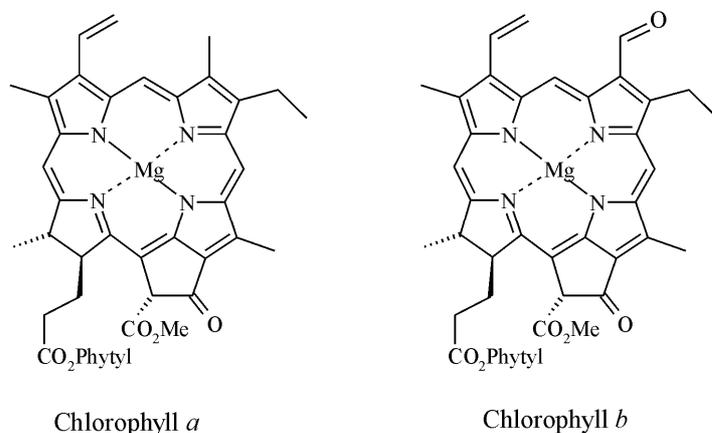
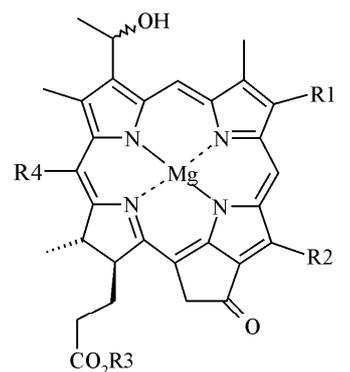


Figure 1: The structure of chlorophyll a and chlorophyll b



R1 = Et, *n*-Pr, *i*-Bu, *neo*-Pent
 R2 = Et, Me
 R3 = Alkyl (various)

Bacteriochlorophyll c R4 = Me
 Bacteriochlorophyll d R4 = H

Figure 2: The structure of bacteriochlorophyll c and bacteriochlorophyll d

Some of the bacteriochlorophylls also exhibit variations in the nature of peripheral substituents (R1-3 in Figure 2). In some cases in excess of 50 individual compounds are possible. Laboratory and field studies indicate that at least some of the structural variations result in response to changes in environmental conditions, including the intensity and spectral profile of the photosynthetically active radiation available to the organisms [5, 6]. Furthermore, various chemical modifications to the pigments occur during senescence (cellular disruption associated with death), during grazing by zooplankton, and as the organic debris in which they are contained sinks through the water column.

Common processes involve replacement of Mg by 2H to form phaeophytins, further loss of CO₂Me to form pyropheophytins and hydrolysis of the phytyl ester to form phaeophorbides. Particular chemical structures formed during these transformations also include **steryl chlorin esters** (SCEs; Figure 3) and oxidation products (e.g. **purpurins**; Figure 4) [4].

Steryl chlorin esters are a class of chlorophyll transformation product in which the sterol moiety is ester-linked to a chlorin carboxylic acid, most often pyropheophorbide *a* (Figure 3). SCEs essentially arise from the grazing of phytoplankton by zooplankton, and occur widely in marine and lacustrine (lake) sediments.

The sterol portion of the SCEs derives from either the algal community or a zooplankton grazer, and is introduced into the pigment structure *via* transesterification. Analysis of sedimentary pigment distributions can, therefore, allow particular environmental conditions to be inferred. As a result of the many transformation processes that affect chlorophyll pigments, their distributions in sediments are often complex, requiring rigorous methods of analysis.

Analysis of chlorophyll pigments

The combination of high performance liquid chromatography (HPLC) using a photodiode array detector (PDA) coupled with atmospheric pressure chemical ionisation (APCI) multistage mass spectrometry (MSⁿ) permits comprehensive qualitative and quantitative analysis of pigment distributions as a linked sequence of events.

The components of the mixture are first separated by HPLC and the electronic absorption spectra of individual chromatographic peaks are recorded using the PDA. As a result of the highly conjugated nature of the pigments, the spectra reveal subtle differences in the nature of the pigment molecules and their transformation products. The eluent passes directly to the mass spectrometer where individual

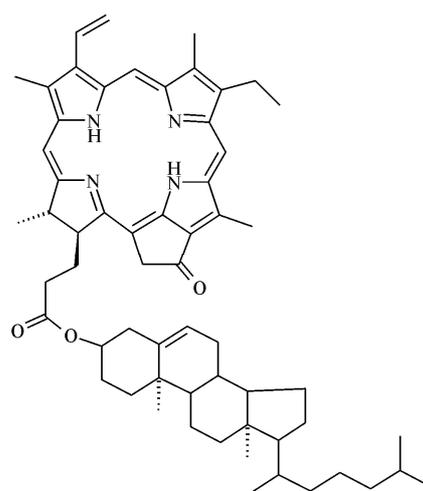


Figure 3: Structure of a chlorin steryl ester (a sterol ester-linked *via* the 3 position to pyropheophorbide a)

analytes are ionised by proton attachment, giving protonated molecules, $[M+H]^+$, that reveal the molecular masses. Individual $[M+H]^+$ ions are selected and subjected to collision-induced dissociation (CID) to produce product ions (the MS^2 spectrum). Any one of the MS^2 product ions can be selected for a further stage of CID to produce a new set of product ions (the MS^3 spectrum). In this way a full mass spectral analysis can be performed within about five stages of CID. The losses observed during CID of chlorophyll and bacteriochlorophyll pigments and their derivatives are highly structure dependent, hence full structure assignment can often be made [7].

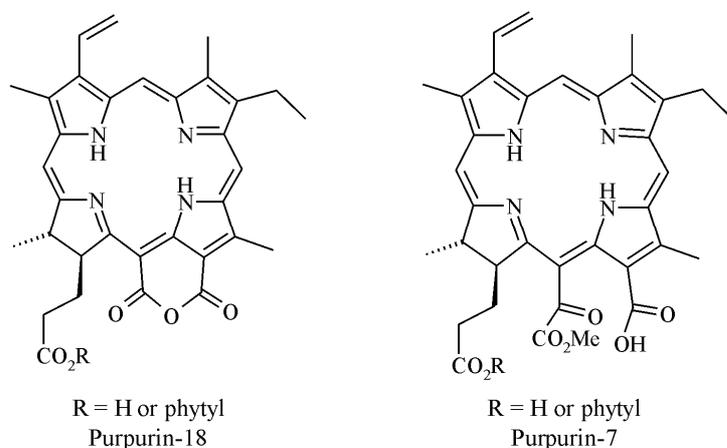


Figure 4: Structures of two chlorophyll oxidation products, purpurin-18 and purpurin-7.

Porphyrin pigments in Antarctic lake sediments

The Larsemann Hills is an ice-free polar oasis in eastern Antarctica, located approximately midway between the eastern extremity of the Amery Ice Shelf and the southern boundary of the Vestfold Hills. At 50 km², it is the second largest of only four major ice-free oases along East Antarctica's 5000 km of coastline. More than 150 freshwater lakes are found in the hills, ranging from small ephemeral ponds to large water bodies such as Progress Lake (10 ha and 38 m deep).

Many low altitude coastal lakes (<15 m) also exist in this region and contain a valuable record of relative sea level changes from which regional ice-sheet history can be inferred. **Kirisjes Pond** is one such small freshwater lake in the Larsemann Hills region.

Pigment analysis of sediment from Kirisjes Pond. A sediment core from Kirisjes Pond, (12 Ha, 9 m depth, altitude 7 m), was obtained by Dr Dominic Hodgson (British Antarctic Survey) with the assistance of the Australian Antarctic Survey. The core was sectioned into 1 cm slices in the field and was kept frozen until analysis. For analysis the sediments were thawed, excess water was decanted and the pigments extracted by sonication in acetone. The sediment core from Kirisjes Pond showed **three** distinct pigment profiles (Figure 5).

Kirisjes Pond -- pigments in the deepest section. The pigments in the deepest section (150 to 112 cm; c. 6525-11195 corr. Yrs BP) (*corrected carbon-dated years before present*) represent a phase during which freshwater conditions existed and supported a community of oxygen-evolving photosynthetic algae. This is indicated by the major pigments being chlorins derived from chlorophylls *a* and *b*, and polar carotenoids typical of oxygenic primary producers, and is supported by the presence of silicate fossils of freshwater diatoms (unicellular algae). Steryl chlorin esters are present in high relative abundance throughout this phase, suggesting an active population of zooplankton grazers was present in the lake. Trace amounts of purpurins indicate oxygenated conditions at the time of deposition.

Kirisjes Pond -- pigments in the middle section. The middle section of the core (94–110 cm; c. 6285–6525 corr. Yrs BP) shows a marked change in the primary producer population. The co-occurrence of bacteriochlorophylls *c* and *d* with chlorophyll *a*-derived pigments indicates the development of a population of photosynthetic bacteria accompanying the algal primary producers.

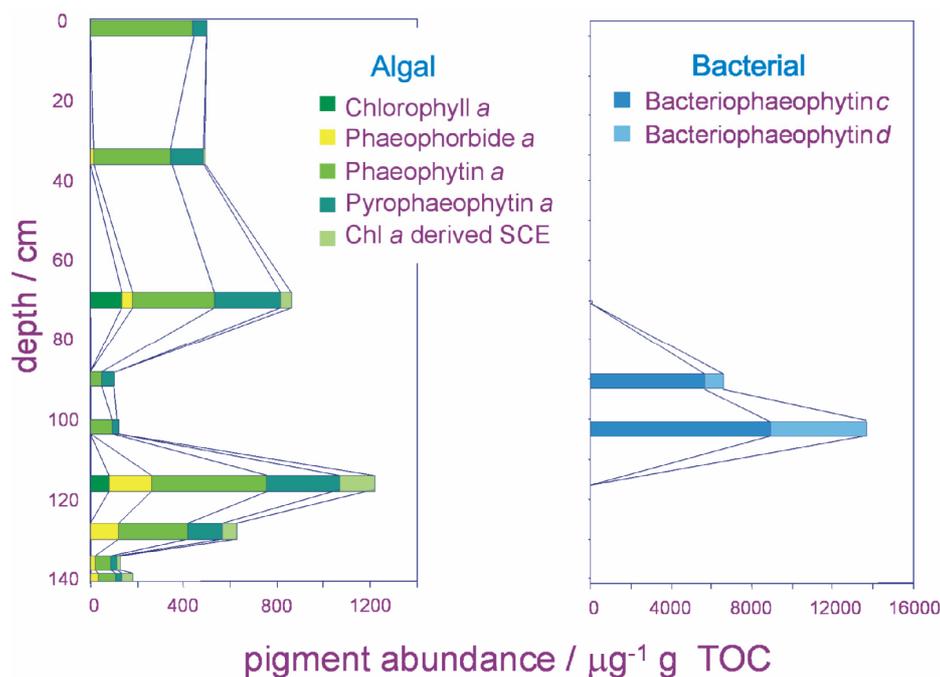


Figure 5: Depth profiles of chlorophyll (algal) and bacteriochlorophyll (bacterial) derivatives in the sediments of Kirisjes Pond, Antarctica

Such bacteria utilise H_2S in photosynthesis in place of H_2O and can only thrive under conditions where the water column is anoxic (excludes all oxygen). The presence of marine diatoms in the sediment indicates that a marine incursion occurred at the time this section was deposited. A subsequent transition zone (88–94 cm; c. 6205–6285 corr. Yrs BP) with a very high abundance of diatom cysts coincides with a shift in the distribution of bacteriopheophytins *c* and *d* homologues to increased alkylation in the macrocycles. This may be related to the extent of development of the anaerobic community and the resultant increase in competition for the available light [5].

The high abundances of bacteriochlorophyll derivatives between 88 and 110 cm and very low abundance of chlorophyll *a* derivatives suggests this period represents development of a planktonic community dominated by anoxygenic photoautotrophs. In such environments grazing is severely restricted and pigment preservation is very good. Thus, aerobic productivity, as judged from the pigment concentrations, was suppressed during the time of the marine incursion.

Kirisjes Pond -- pigments from the uppermost section. The uppermost section of the core (surface--88 cm; c. present to 6205 Yrs BP) records a return to freshwater conditions with a dominance of oxygenic photosynthetic organisms. Freshwater diatoms are present and the major pigments are derived from chlorophylls *a* and *b*.

Differences between the two freshwater phases. A notable difference between the two freshwater phases is observed in the chlorophyll transformation products. While the total abundances of chlorophyll *a* and *b* components are approximately the same for both phases, significant variations in the distributions of the various transformation products are evident. Steryl chlorin esters are much less abundant in the upper phase, indicating a less well-developed community of grazers. The wider range of sterols present among the SCEs, with a greater relative contribution from sterols with 27 and 28 carbons, indicates a shift either in

the primary producer community or the grazing community.

The non-SCE chlorophyll transformation products make a greater relative contribution to the total pigment distribution and the level of purpurins was higher than in the initial freshwater phase. Together, these features are suggestive of a greater proportion of the pigment distribution originating from dead and senescent cells than from deposition *via* faecal material as would be expected during times of greater grazing activity.

Sea level changes and porphyrin distribution. The dramatic difference in the pigment profile in the middle section of the core can be explained as a consequence of change in relative sea level. As relative sea level increased the lake basin would have been inundated by marine waters. These waters would have contributed an increase in the sulfate levels in the lake, stimulating sulfate reducing bacteria in the lake bottom waters and/or sediment (Figure 6).

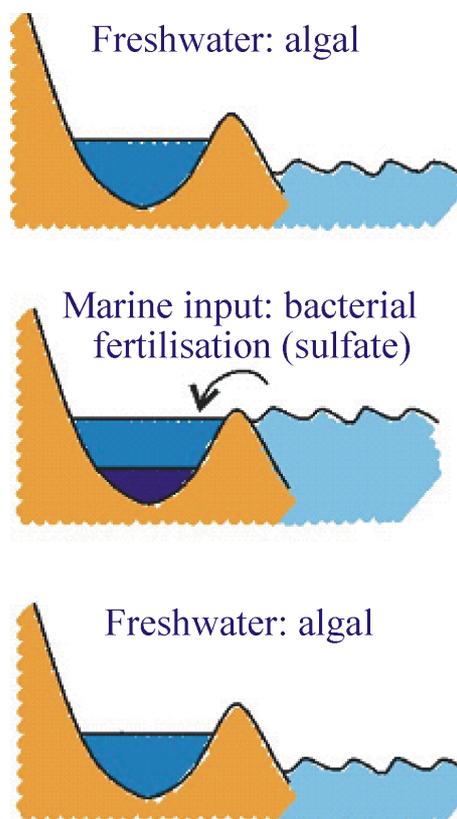


Figure 6: Diagram representing the three main stages in the evolution of Kirisjes Pond over the last 11,000 years (adapted from Squier, 2003, reference 8)

Sulfate reducing bacteria decompose organic matter by oxidation using sulfate as the source of oxidising power, thereby reducing the sulfate anions. The activity of the sulfate reducers would, in turn, have stimulated the photosynthetic bacterial community by supplying the H_2S required for their photosynthetic activity. Increasing levels of H_2S in the water column and increased consumption of oxygen through oxidation would have led to a stratified water column with algal photosynthesis being restricted to the oxygenated surface waters and with bacterial photosynthesis being prevalent within the anoxic deep waters of the lake. The absence of oxygen in the deep waters is reflected in the profiles of chlorophyll *a* oxidation products throughout the core.

Following a decrease in sea level around 6285 years ago, the lake reverted to a freshwater system dominated once again by algae. Notably, however, the activity of grazing organisms appears to have failed to reach previous levels and appears to have been eliminated during the more recent history of the lake. Chlorophyll oxidation products are detected in significant abundance only in the bottom and top sections of the core. Their presence only at very low levels in the middle section confirms the development of extensive water column anoxia during the period of connection to the ocean.

Conclusion

Porphyrin pigment distribution found in cores from several other lakes in the region also reveal periods of connection with marine waters at similar times. Thus, the variation in relative sea level was a phenomenon that affected the whole of the region. The pigments are particularly useful markers of these environmental changes as they can be monitored readily, reflect all of the main groups of primary producers (unlike many fossil remains), and allow sediment records to be profiled at high stratigraphic resolution to generate records that have excellent time resolution.

Acknowledgement

The work described in this article formed part of the PhD studies of Angela Squier and was carried out in collaboration with Dr Dominic Hodgson of the British Antarctic Survey.

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This article is based on a presentation by Dr Keely at the ECG's 2007 Distinguished Guest Lecture and Symposium 'Environmental Chemistry in the Polar Regions'.

Free radicals at high latitudes

Free radicals are chemical species which contain one or more unpaired electrons and thus are highly reactive. Free radicals are at the heart of the chemical cycles that process natural and anthropogenic emissions. Understanding atmospheric free radical chemistry, both in qualitative and quantitative terms, is essential for the construction of models of future changes to the atmosphere (and to the climate), as **Prof. Dwayne Heard** explains.

Introduction

Calculating the future change in the composition of our atmosphere is performed using complex climate change and air quality models. These

models require the following information:

1. The future emissions into the atmosphere from anthropogenic and biogenic sources. A precise knowledge of such emissions is, of course, unknown, and assumptions have to be made using various emissions scenarios.
2. Meteorological parameters, which control the mixing of emissions into the background atmosphere and effect long-range transport, for example wind velocities and larger atmospheric circulations.
3. The detailed chemistry that controls the oxidative removal and processing of emissions via atmospheric free radical chemistry and photochemistry.

Emission control legislation, which globally is costing billions of dollars, is driven by model predictions so it is important that the inputs to the model are correct. We cannot wait to find out if the predictions are accurate. In order to probe whether the chemistry and

photochemistry are faithfully represented by the model, we can use the chemical model to calculate key chemical intermediates that we can measure now.

Free radical chemistry in the atmosphere

Free radicals are ideal target species for atmospheric modelling, as their lifetimes are short (a few seconds) and their concentrations are influenced by the local *in situ* chemistry, and not by transport.

Hydroxyl radical chemistry

The hydroxyl radical (OH), often referred to as the “detergent” of the atmosphere, reacts with virtually all trace species, regulating their concentrations and atmospheric lifetimes. Examples of species controlled by OH include CO and benzene (toxic substances), CH₄ and HCFCs (greenhouse gases), hydrocarbons (smog precursors), oxygenated VOCs (precursors to

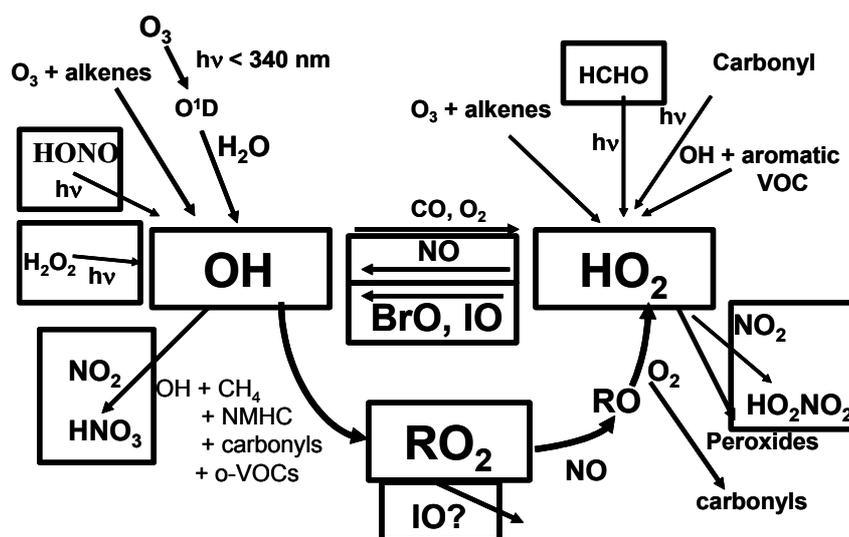


Figure 1: OH, HO₂ and RO₂ radical chemistry in the polar boundary layer

secondary organic aerosols) and SO₂ and NO₂ (precursors to acidification).

It is important to measure OH as its concentration defines the oxidising capacity or self-cleansing capacity of the atmosphere, particularly in the daytime, and any trends are critical. OH is intimately involved in all aspects of the chemistry related to climate change and air pollution – and hence is an ideal target molecule for modelling. If a model can predict the concentration of OH successfully, we then have confidence that the chemistry is correct.

Free radical chemistry in polar regions

Free radicals are generated by solar photolysis and until recently it was thought that areas of low insolation, such as the polar regions, were chemically rather barren. Models indicate that for the greenhouse gas methane, hardly any oxidation by reaction with OH occurs in the polar regions. However, recent fieldwork in polar regions has revealed elevated levels of free radicals (e.g. OH, HO₂, RO₂, IO and BrO), demonstrating the potential for significant chemical processing.

IO and BrO radicals are generated from reactions of I and Br atoms with ozone. The halogen atoms arise from the photolysis of photolabile halogens emitted from sea-weeds and other marine organisms. IO and BrO radicals can perturb the NO₂/NO and HO₂/OH ratios, and hence the oxidizing capacity

of the atmosphere, as well as being involved in ozone depletion episodes and the oxidation of elemental mercury. **Figure 1** summarizes the atmospheric chemistry of OH radicals.

Measurements of atmospheric free radicals

The measurement of atmospheric free radicals is a difficult experimental challenge. The concentration of OH at noon is $\sim 10^6$ molecule cm⁻³ (mixing ratio of 1 part in 10¹⁴) and the lifetime is < 1 second. For other radicals, RO₂, IO, BrO the concentrations are slightly larger at $\sim 10^8$ molecule cm⁻³, or a few

parts per trillion. Techniques developed for their detection must be very sensitive, highly selective, and have good spatial and temporal resolution. In polar regions these radicals have been detected using laser-induced fluorescence (LIF; OH, HO₂ after conversion to OH and IO), long-path differential optical absorption spectroscopy (DOAS; BrO, IO) and chemical ionization (CI) mass spectrometry (HO₂ + RO₂, OH).

Here at Leeds University both the LIF and DOAS methods have been deployed in polar regions, and the reaction sequence used to describe OH radical is the Master Chemical Mechanism.

Hydroxyl radicals in the polar regions

Measurement of hydroxyl radicals. The first measurements of OH radicals in the polar regions were made at Palmer station on the Antarctic peninsula, during the SCATE campaign. Because the hydroxyl radicals were removed from local sources of halogen species, the chemistry behaved as expected for a remote pristine environment. The OH concentrations were very low (mean 24 hour [OH] = 1.1×10^5 molecule cm⁻³, solar noon [OH] $\sim 5 \times 10^5$ molecule cm⁻³), and there was good agreement (30%) with a model calculation,

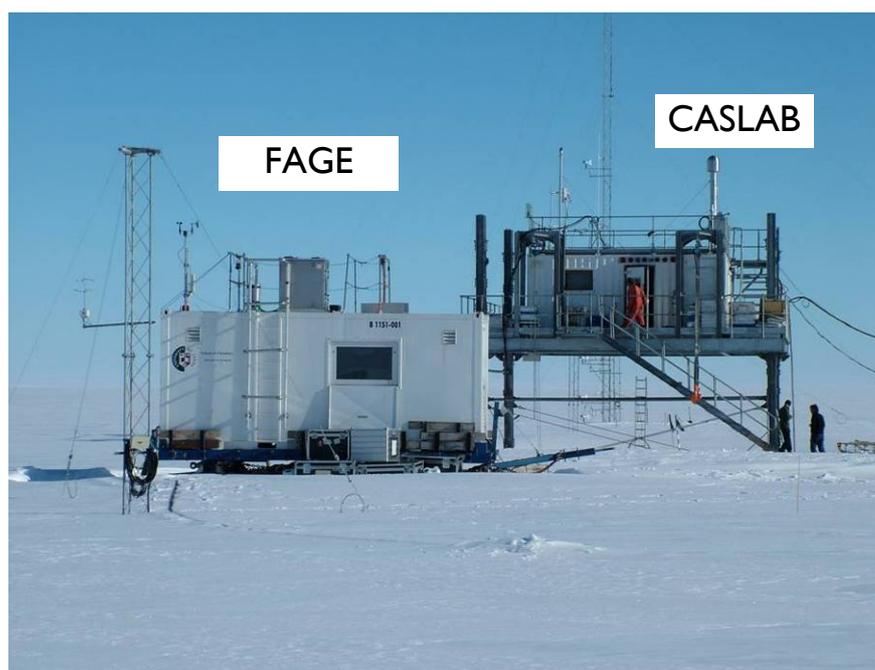


Figure 2: The Leeds FAGE instrument for the measurement of OH and HO₂ radicals situated adjacent to the Clean Air Sector Laboratory at the Halley Station, Antarctica.

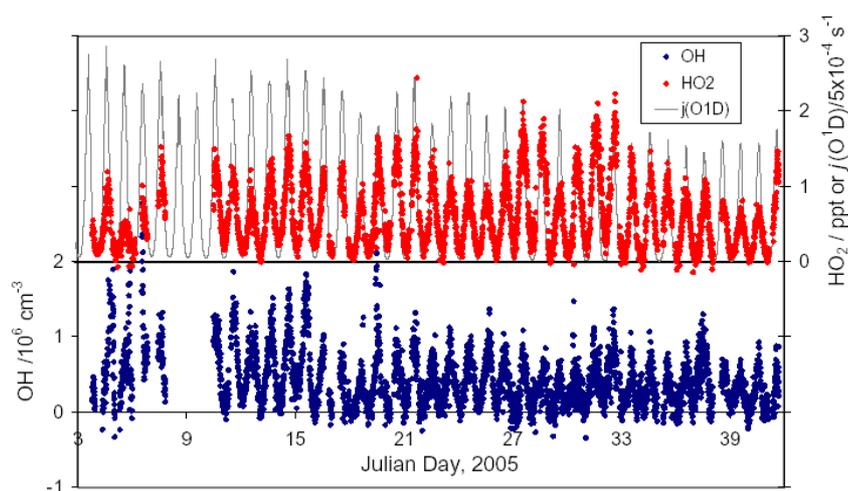


Figure 3: Concentrations of OH and HO₂ radicals measured during the CHABLIS summer intensive January-February 2005 at Halley Base, Antarctica. $j(\text{O}^1\text{D})$ is the photolysis frequency of ozone to form O(¹D) atoms. See Bloss et al, *Atmos. Chem. Phys.*, **7**, 4171-4185, (2007) for further details.

showing that OH production was dominated by ozone photolysis followed by the reaction $\text{O}(\text{D}) + \text{H}_2\text{O}$, and its loss by reaction with CO and CH₄. These measurements can be taken as a “base case”.

Hydroxyl radical chemistry influences measured OH concentrations. Measurements of OH and HO₂ + RO₂ radicals taken at Summit Greenland (3207 m on the central plateau) showed a perturbation of the chemistry due to snow emissions of NO_x and other oxidant precursors, for example formaldehyde (HCHO), hydrogen peroxide (H₂O₂) and nitrous acid (HONO), which are expected to augment levels of OH and HO₂.

One mechanism for the production of HONO and NO_x from snow is the photolysis of nitrate ions in the surface layer of snow. Difficulties were encountered in reproducing the measured levels of free radicals, partly due to uncertainties in the concentrations of key species, for example HONO, and unmeasured sources and sinks. Higher levels of OH were observed when air masses were being rapidly transported from coastal Greenland, providing some evidence for a possible influence of halogen chemistry.

Nitrogen oxides measurements at the South Pole

There have been several field campaigns at the US-operated South Pole base, in which concentrations of free radicals have been measured. The results were most surprising. Elevated levels of nitric oxide [NO] = 100-200 pptv were observed, much higher than expected for a pristine, remote environment, but caused by snowpack emissions into a very shallow boundary layer (only a few 10s of m).

The higher NO concentration (**Figure 1**) can accelerate the catalytic cycles which regenerate OH, leading to elevated OH up to $1\text{-}2 \times 10^6$ molecule cm^{-3} . As there is 24 hour sunlight at the South Pole, the oxidizing capacity in this shallow layer over much of Antarctica is higher than in the tropics! As for Summit Greenland, emissions of HCHO and H₂O₂ also contribute to enhanced photochemical activity, accounting ~ 25-30% each towards the production of OH and HO₂.

Novel measurements of nitric acid (HNO₃) and pernitric acid (HNO₄) showed these species play an important role in the redeposition of nitrogen to the snowpack. In addition, because of the elevated NO, the rates of reactions HO₂ + NO and RO₂ + NO producing NO₂ were fast, which generates *in situ*

ozone following photolysis of ozone. Recent aircraft and balloon measurements from South Pole indicated that the enhanced production of ozone is quite widespread in the boundary layer above the Antarctic plateau. Despite a comprehensive set of measurements, models typically overpredicted OH concentrations, suggesting some misunderstandings of the chemistry still remain.

Measurements of hydroxyl and hydroperoxyl (HO₂) radicals during the CHABLIS campaign

The CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) campaign took place at the Halley Station, Antarctica. OH and HO₂ radicals were measured *in situ* by LIF at low pressure (the FAGE technique) for a 2 month-intensive (January – February 2005), and BrO and IO radicals were measured year-round by DOAS, using an 8 km (2 x 4 km) light path ~4 – 5 m above the snowpack. Extensive coupling between these species was observed.

Halley is located on the floating Brunt Ice Shelf ~ 15 km from the ocean edge at 76 S, 26 W. The ice shelf is ~ 35 m thick and is moving at ~ 500 m per year. Local ice leads open up in the spring and summer months. The CHABLIS project was led by the British Antarctic Survey, but involved five UK Universities, and a wide range of trace gases and radiative parameters were measured. The FAGE instrument is housed in a shipping container and was positioned adjacent to the Clean Air Sector Laboratory (**Figure 2**). The container was unloaded from the supply ship onto the ice-shelf in December 2004, but by mid-late February 2005 the local ice conditions for that particular year made it impossible to load the container back onto the ship. Instead it was towed ~ 50 km over the ice to N9, an alternative loading site, and lifted back onto the ship, with undercut ice making the procedure rather precarious!

The depth of the mixed boundary layer is considerably larger at Halley than at South Pole, and so although there are still significant snow emissions, the concentration of NO_x and HCHO is

lower (mean NO = 8 ppt, NO₂ = 5 ppt). Measurements of OH and HO₂ taken over 37 days, with OH up to 2.5 × 10⁶ molecule cm⁻³ observed early in the intensive period as shown in **Figure 3**. The relationship between [OH] and the photolysis frequency of ozone, *j*(O¹D), was found to be:

$$[\text{OH}] / 10^5 \text{ cm}^{-3} = 2.52 \times \{j(\text{O}^1\text{D}) / 10^{-5} \text{ s}^{-1}\}^{0.74} + 1.06$$

with the less than linear relationship indicating considerable recycling of HO₂ to OH mediated by reaction with NO, IO and BrO radicals (the latter both ~ 5 pptv in the summer). The non-zero OH when there is no photolysis of ozone indicates that OH is still generated by other processes, for example photolysis of HONO at considerably longer wavelengths.

The spring peak in BrO and IO (October) was ~ 20 pptv for both species, some of the highest levels ever recorded. These elevated levels are consistent with recent measurements of IO in this region from space. The IO and BrO are strongly correlated with local wind-direction and trajectory air-mass origins, and the highest concentrations were seen when air was sampled from the open ice front sector, where frost flowers are known to exist, providing one possible mechanism (but there are also others) for the production of short-lived halogen species.

The main sources of HO_x were the photolysis of O₃ and HCHO, with important but uncertain contributions from HONO and higher aldehydes. CO and CH₄ were the main sink for OH but model calculations suggest that other OH sinks are present, possibly oxygenated VOCs. The effect of BrO and IO on concentrations of OH and HO₂ at Halley is quite striking. **Figure 4** shows the calculated mean diurnal variation of the principal OH production mechanisms over the measurement period. The largest source of OH is the photolysis of HOI, with HOBr photolysis also important. HOI and HOBr are generated from the reactions HO₂ + IO and HO₂ + BrO, respectively. HONO is also an important but uncertain photolytic source of OH, and high quality HONO measurements are required.

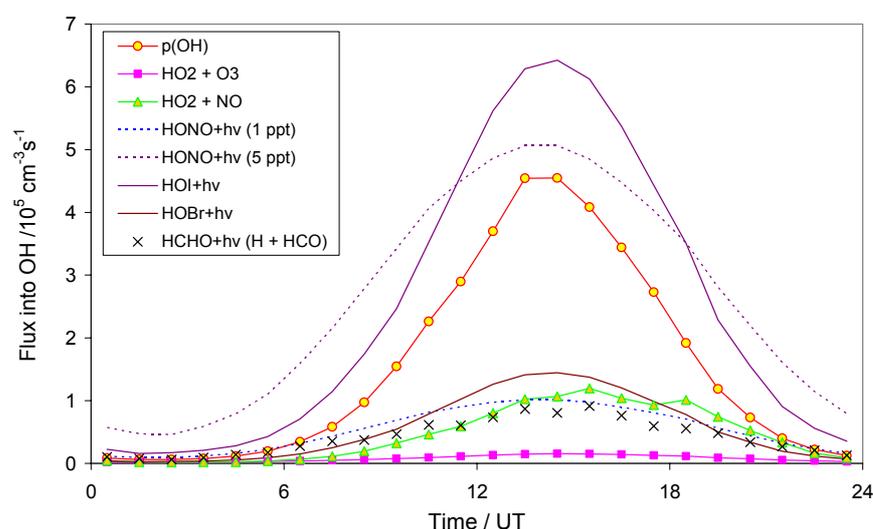


Figure 4: Mean diurnal profile of the rates of the major production routes for OH radicals during the CHABLIS summer intensive, 2005. *p*(OH) is production from the reaction O(¹D)+H₂O with O(¹D) coming from ozone photolysis. See Bloss et al, *Atmos. Chem. Phys.*, **7**, 4171-4185, (2007) for further details.

Conclusion

There is now a considerable database of free radical measurements at high latitudes using a range of techniques. Free radicals are ideal targets to test the accuracy of chemical mechanisms. Oxidation chemistry mediated by OH is more complex than expected for a remote, pristine environment. Snow emissions of radical and NO_x precursors increase the oxidising capacity of polar environments, and halogens control all important aspects of the chemistry of the coastal Antarctic boundary layer at Halley during the summer months.

A key question is the vertical extent of halogen influence on the oxidative chemistry of polar regions. Recent satellite measurements suggest that elevated levels of IO exist throughout the boundary layer. Further fieldwork is planned in 2008 in the Arctic (Hudson Bay) to further investigate ozone depletion events, and the role of halogen species on the oxidative chemistry of the polar boundary layer.

Acknowledgements

I would like to thank Dr. James Lee (York University) and Dr. William Bloss (University of Birmingham) who operated the Leeds FAGE instrument at Halley during the CHABLIS project, and other members of the CHABLIS consortium.

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This article is based on a presentation by Prof. Heard at the ECG's 2007 Distinguished Guest Lecture and Symposium 'Environmental Chemistry in the Polar Regions'. Other presentations from this meeting were published in the July 2007 issue of the ECG Bulletin.

Other accounts of the work at the Halley Station, Antarctica and the CHABLIS campaign appeared in issues of the ECG Bulletin published in July 2004, July 2006, and July 2007 respectively

Ozone hole paradigm is challenged by a new laboratory measurement of the chlorine peroxide spectrum

New data published in 2007 on the rate of photolysis of chlorine peroxide (Cl₂O₂) have cast doubts on the accepted mechanisms of ozone depletion in the stratosphere. **Francis Pope** compares the published kinetic analyses of the breakdown of Cl₂O₂ and comments on the significance of these measurements.

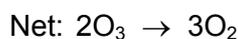
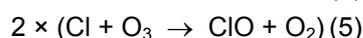
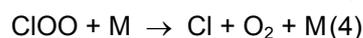
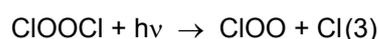
Introduction

Since 1985 when Farman and his colleagues first discovered the Antarctic ozone hole [1], great effort has been made to elucidate the mechanisms responsible for the loss of polar stratospheric ozone in both the Arctic and Antarctica.

The mechanism generally accepted to be largely responsible for polar ozone loss involves catalytic chlorine oxide (ClO_x) species (**Box 1**). The cycle was first proposed by Molina and Molina and, according to the current consensus, accounts for around 60% of ozone loss [2].

Chlorine peroxide, ClOOCl, is a crucial intermediate in this cycle. High concentrations are built up during the

cold and dark polar winter as an active chlorine reservoir. When spring arrives, solar radiation of suitable wavelengths reaches the stratosphere with which ClOOCl photolysis can occur, yielding two ozone destroying chlorine atoms. The photolysis rate of ClOOCl is critical to the efficiency of this scheme. The faster the ClOOCl photolysis, the greater is the fraction of ozone loss that can be attributed to the catalytic cycle shown in **Box 1**.



Box 1: ClO_x catalysed ozone destruction

Determination of ClOOCl photolysis rate

The photolysis rate is dependent on the wavelength integrated product of the ClOOCl absorption cross sections, the quantum yield of ClOOCl, and the flux of available light. Many measurements of the ClOOCl cross sections have been attempted previously. However, in the atmospherically important wavelength range, 300 – 500 nm, significant

discrepancies exist between the different experiments. The ClOOCl molecule is difficult to generate, store and use. These factors make the determination of the absorption cross sections of ClOOCl very challenging. Additionally, synthesis must be performed *in situ* because the ClOOCl molecule is weakly bound and only stable at low stratospheric temperatures.

Several methods of ClOOCl synthesis have been described in the literature. Unfortunately, all synthetic routes result in the co-production of spectral impurities. Therefore, subtraction of the spectral impurities from the experimentally recorded spectrum must be performed to retrieve the true ClOOCl spectrum. The differences in the chosen methods of subtraction are probably the biggest cause of discrepancies between spectra in the literature. Many experimental data sets also suffer from poor signal to noise due to small concentrations of ClOOCl used in the measurements.

The recent work of Pope *et al* [3] generated much higher concentrations of ClOOCl than previously attained by other studies. Dramatic reductions in spectral impurities were also achieved using a novel step in the synthesis. Subsequent to generation, the ClOOCl was collected in a cold trap with its spectral impurities. After collection, gradual heating of the trap resulted in

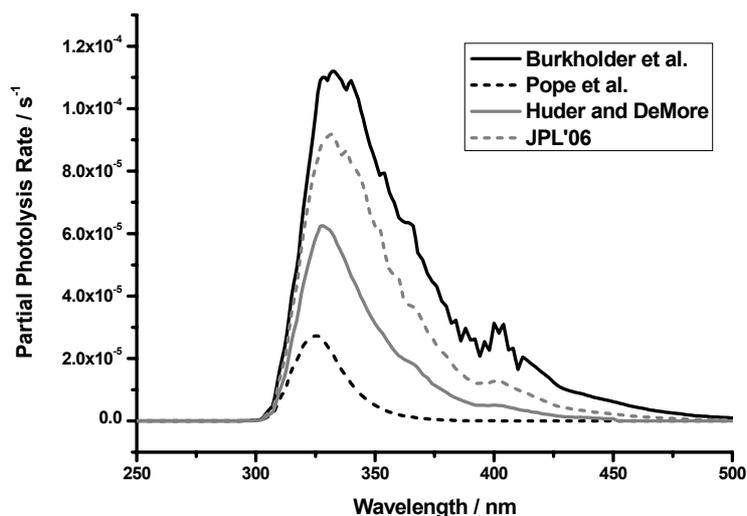


Figure 1: Calculated partial photolysis rates of ClOOCl using different determinations of the absorption cross sections

species leaving the trap at different times, depending on their volatility. Complete separation was not possible and spectral subtraction was still required, albeit at much lower levels than other work. The resulting Pope *et al* ClOOCl spectrum has absorption cross sections values significantly lower than other studies [3].

Atmospheric implications of the Pope *et al* data set

The Pope *et al* absorption cross sections [3] strongly affect the calculated ClOOCl photolysis rates. **Figure 1** shows the partial photolysis rates calculated for a typical Arctic polar vortex for several different evaluations of the ClOOCl cross sections. Additional parameters used in the calculation were as follows: solar zenith angle of 86° , 20 km altitude, and typical O_3 and temperature profiles. **Figure 1** illustrates, visually and quantitatively, the difference between new and previously measured cross sections.

The integrated area under the curves represents the total photolysis rate. Total photolysis rates reported in references [4], [5] and [6] are respectively 8.9, 6.2, and 3.5 times larger than the Pope *et al* evaluation [3]. The Burkholder *et al* data set [4] is the largest valued data set in the literature. The data from Huder and DeMore [5] is used as the basis for the IUPAC recommendation. The Jet Propulsion Laboratory 2006 evaluation

[6] is an average of various studies. The Burkholder *et al* data set [4] allows for the greatest agreement between modelled and measured O_3 loss. Use of smaller cross sections reduces the modelled O_3 loss.

The calculated ozone loss that results from the inclusion of the lower Pope *et al* absorption cross sections leads to a severe underestimation of the observed O_3 loss. This underestimation is too large to allow for the possibility of adjustment of other model parameters. The result is also not model-specific, with the same outcome obtained from several different models [7]. If the Pope *et al* cross sections are correct, then the currently accepted chemical mechanisms of O_3 loss are incomplete. This result is controversial and has led to perspective pieces in both *Nature* [8] (see p. 27 below) and *Science* [9].

Future work and open questions

Clearly the controversial data of Pope *et al* must now be verified or refuted, necessitating further experimental studies. The new experimental techniques developed in the Pope *et al* study eased some of the difficulties that marked previous studies. Is it possible to synthesise ClOOCl at higher purities than even those attained in the Pope *et al* study? If this does not prove feasible, then independent verification of spectral impurities, and in particular the troublesome Cl_2 , might yet be achieved. If the Pope *et al* absorption

cross sections prove to be reproducible, then the hunt for the missing mechanism will begin in earnest. What are the possibilities for missing mechanisms? Reasonable candidates could be evaluated in atmospheric models before experimental work begins. It is likely that some species and schemes have already been considered, but might need to be revisited.

Summary

The absorption cross sections of ClOOCl have been measured multiple times, with widely varying values in the atmospherically important wavelength window. New work by Pope *et al* generated purer and higher concentrations of ClOOCl than were previously attainable. Their measurements yielded controversially low values for the ClOOCl absorption cross sections. If correct, the new results necessitate rethinking the mechanism that generates the ozone hole. Future experimental work is now required so that consensus on the correct cross sections may be reached.

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Greener chemical manufacturing

Professor James Clark, Director of the Green Chemistry Centre at the University of York, describes some of the new technologies that are emerging for chemical manufacturing as a result of the impact of increased raw materials and energy costs, new legislation, and environmental considerations.

Introduction

The chemical industry is under an unprecedented degree of pressure. Chemical manufacturers, suppliers and users face drivers to change at every stage in the supply chain:

- Market distortions in raw material price and availability due to the emerging mega-industries in the East
- Rapidly increasing oil prices affecting the feedstocks for over 90% of all organic chemicals and all chemical manufacturing
- Ever tighter legislation and punitive charges over hazardous chemical storage and waste disposal
- Increasing public and NGO pressure on chemical manufacturing and increasingly on

chemical products. An exponential growth in chemical related legislation now especially affecting chemical substances (notably REACH).

While the 1990s saw a period of "good housekeeping" in the industry to improve the basic operating procedures, operator health and safety and relatively easy to deal with problems, there is a growing recognition that more changes are required including the introduction of new, cleaner technologies and careful examination of supply chains [1,2]. Examples of how industry, often in partnership with the research base, is addressing these challenges cover evaluation methods and technological solutions at all stages in the product supply chain. Some examples are described here.

Measuring green – Green Chemistry Metrics

The adage that if you can't measure it, then you can't fix it certainly applies to chemical production. One of the most important industry-led developments in greener chemical manufacturing in the last ten years has been the introduction of green chemistry process metrics [3]. It is now widely recognised that the measurement of yield alone is insufficient for reporting on process efficiency since it neglects process auxiliaries such as solvent, reagents and

catalysts as well as the washing water, extraction solvent, drying agents, etc used to isolate the product.

One example of a green chemistry process metric is mass efficiency, which can be expressed as mass of final product divided by the total mass of all input materials. Very low mass efficiencies are currently found in higher value chemical manufacturing such as pharmaceuticals and speciality chemicals where multi-stage complex syntheses are used.

Green Chemistry Metrics can help to reveal major process inefficiencies such as high solvent usage or non-renewable reagents. Even these metrics may be inadequate since they tend not to include energy which in environmental and at today's prices, economic terms is unreasonable. More sophisticated environmental footprinting will include energy consumption and can also cover extended manufacturing processes for example going beyond the primary manufacture of the active pharmaceutical ingredient to include the (secondary) manufacture of the fully-formulated products (e.g. tablets) and including packaging. In this way, chemical manufacturing companies will be able to better rectify hot spots of low resource efficiency, high waste or other specific problems.

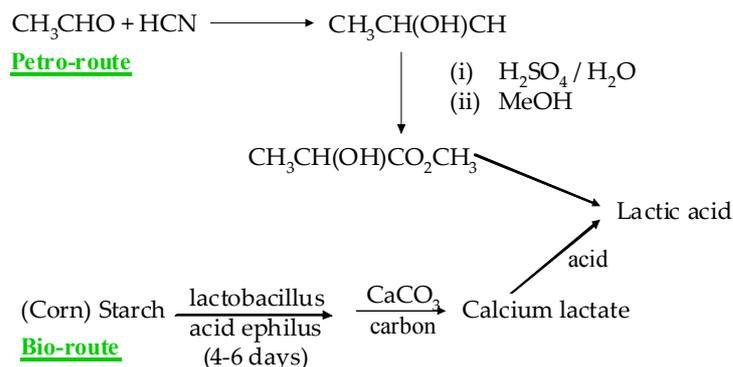


Figure 1: A conventional and a 'green' production route to lactic acid

Renewable resources

While over 90% of the organic chemical products on the market today are petroleum-derived, there is a rapidly growing interest in the use of alternative renewable resources, notably biomass. One of the best new commercial examples of this is bio-derived lactic acid, used now in large quantities for the manufacture of poly(lactic acid) [4]. 'Bio-lactic' acid is manufactured by NatureWorks L.L.C. (<http://www.natureworkslc.com/>) in a fermentation process starting with corn (Figure 1). One immediate concern with this is the competitive use of land and crops for non-food versus food production. In fact, lactic acid (as well as many other future biomass-derived building blocks chemicals) can also be made from waste biomass as has recently been demonstrated using sugarcane bagasse (India alone produces 45 million tonnes of this every year) [5]. In other respects the NatureWorks lactic acid manufacturing process appears to be a very good example of green chemistry: unlike the petrochemical based route, it is based on a renewable resource and from a wider environmental footprint perspective has few process hotspots.

Future biorefineries like the petroleum refineries of today will have energy as their main product(s). The sustainable chemicals of tomorrow can come from a relatively small fraction of the refinery turnover similar to petrochemicals today. Solvay has

already demonstrated how a biofuel by-product can be used to make a chemical product that might be considered to be economically as well as environmentally beneficial [1]. The commodity chemical epichlorohydrin is made by a selective chlorohydroxylation-dehydrochlorination process starting from the glycerine by-product from biodiesel manufacture, although the environmental benefits of at least some biodiesel feedstocks have been brought into question. It is important that green chemistry is flexible enough to take advantage of such opportunities, even if they don't always turn out to be viable in the long term.

Cleaner Production

Green Chemistry Metrics can be used to identify the most wasteful chemical reactions. The simplest of these, Atom Economy, the sum of the molecular weights of the substrates divided by that of the desired product, shows large differences between a simple $A + B = C$ reaction (e.g. Michael addition, hydrogenation) and those where only a small part of one or more of the substrates is incorporated in the desired product (e.g. oxidations using stoichiometric heavy metal oxidants and fluorinations using quaternary ammonium fluorides).

By using more elaborate metrics such as Mass Efficiency and E Factor, reactions that use large quantities of high molecular weight catalysts (e.g. AlCl_3 in Friedel-Crafts acylations) and reactions that require protection/deprotection agents and activating groups (e.g. in amidations) are also exposed as especially wasteful.

Evaluations such as these helped a consortium of the world's largest pharmaceutical manufacturers to prioritise common reaction types that need greening. The priorities included amide formation (without poor atom economy reagents such as acid activating groups) oxidations (without chlorinated solvents), Friedel-Crafts reactions (without stoichiometric "catalysts"), fluorination (with lower environmental impact non-hazardous processes) and reduction (without hydride reagents) [6].

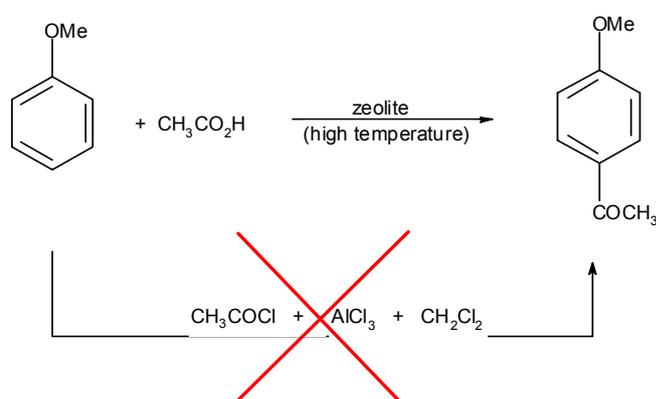


Figure 2: A safer, 'green', alternative for a Friedel-Crafts acylation

One of these where progress at an industrial scale has been made is Friedel-Crafts acylation using a recoverable and safe-to-handle catalyst rather than a non-renewable and hazardous Lewis acid [7].

The zeolite route (**Figure 2**), developed by Rhodia shows dramatically improved green chemistry metrics (compared to the traditional AlCl_3 route including a much lower E Factor and higher atom efficiency), as well as avoiding hot spots such as the use of a halogenated solvent and a dangerous reagent. However, the low activity of the zeolite catalyst limits effective reactions to those of activated substrates, and a more active "green" catalytic system is urgently needed.

Commercial progress has also been made with epoxidation reactions which represent one of the versatile ways of activating alkenes. With small molecules, the solid titanium silicate catalyst TS-1 developed by Enichem is very effective (**Figure 3**) [7]. The reaction has excellent green chemistry credentials with the use of a solid, renewable catalyst, a relatively benign and atom efficient oxidant and only water as the co-product:

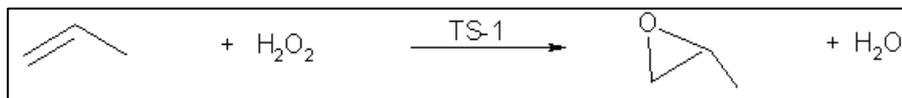


Figure 3: Titanium silicate catalysed alkene epoxidation

This can be considered to be a greener alternative to the commercially established but less atom efficient route based on organic hydroperoxides and transition metal catalysts [7].

Larger pore versions of the TS-1 catalyst show promise for future applications with larger molecules. Noyori's chlorinated solvent-free and peracid-free epoxidation system (**Figure 4**) also lends itself to larger substrates and can be useful for higher value products such as fragrance and pharmaceutical intermediates [7].

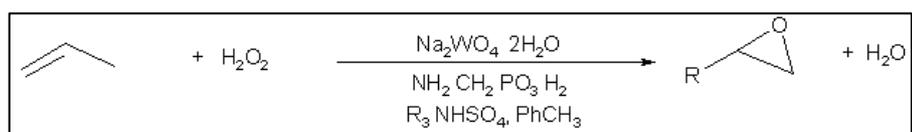


Figure 4: A non-peracid and non-chlorinated solvent method for alkene epoxidation

New Green Technologies

The use of non-fossil feedstocks for chemical manufacture, alternative routes to important chemical products and the use of novel catalysts such as solid acids and porous solids represent step changes in reducing the environmental impact of chemical manufacturing. The associated reaction engineering is however, often conventional, e.g., batch type reactors or established continuous flow processing. A good example of novel, so-called "intensive processing" is the use of spinning disc reactors whereby the reaction fluids (e.g. a solution of substrates) are fed onto a rapidly spinning disc (which may have a catalytically active surface) [8] which can be heated or cooled. One of the key features is the short residence time in the reaction zone, reducing process hazards but limiting the technology to fast reactions. The most promising non-VOC solvent technology is supercritical fluids and especially supercritical carbon dioxide (scCO_2) which is already proven on an industrial scale for extraction, e.g. decaffeination, and is now being reported in industrial

strong, typically acid catalyzed). Here industrial development is progressing through industry-academic partnerships such as that involving Merck [10].

Another step-change technology that may be about to become widely used in chemical processing is microwave activation including microwave assisted organic reactions. While the technique has been a popular academic subject for a number of years, clear evidence for improved energy efficiency in chemical synthesis [11] has only recently been reported, and the emergence of a number of large scale microwave reactor manufacturing companies may open the ways to future large scale chemical manufacturing based on very short reaction times [12].

Conclusion

Unprecedented pressures for change across all stages in the lifecycle of chemical products provides a unique platform for the development and application of cleaner technologies that are more sustainable and reduce the overall environmental footprint of chemical products.

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Biographical Note: James Clark has an international reputation for his work in green chemistry and was a founding director of the Green Chemistry Network at the University of York. He was also the founding Scientific Editor for the RSC journal *Green Chemistry*, and is an author of numerous books on green chemistry. He now holds the Chair of Industrial & Applied Chemistry and heads the Green Chemistry Centre at York, which integrates green chemistry research, industrial collaboration and educational developments and issues relevant to the public understanding of science. He is also the Director of the Green Chemistry Centre of Industrial Collaboration. His research interests include heterogeneous catalysis and supported reagents, and the exploitation of renewable resources.

DEBATE: Is the teaching of the science of global warming and climate change flawed?

In January 2007 the Chief Executive of the Royal Society of Chemistry, **Dr Richard Pike**, issued a widely-circulated press release on climate change. The aim of this statement, which is reproduced below, was to encourage better teaching of the science behind climate change. However, Environmental Chemistry Group member, **Dr Janet Moxley**, was concerned that the ‘four key facts’ on the environment explained in this press release, which ‘children should know’, were themselves a distortion of the true position. We therefore invited Dr Moxley to present her point-by-point rebuttal of Dr Pike’s press release. To conclude this dialogue, we also append Dr Pike’s reply to Dr Moxley’s comments.

“Teaching of global warming flawed”, says chemistry chief

Climate change and global warming teaching in schools is flawed through omission, simplification and misrepresentation, says the Royal Society of Chemistry’s chief executive. “The problem needs to be addressed if the UK is to play a key role in tackling the issues raised, and exploiting related business opportunities,” says **Dr Richard Pike**.

He added: “These deficiencies are partly the result of needing to give youngsters easily digested concepts, but many teachers now agree that in doing so there is the risk of losing sight of the bigger picture.” That picture is not being articulated because of the very limited, quantitative references to climate change in school text books, if at all, says the head of the 43,000-member society.

“Support from web-based organisations is making progress, but is fragmented and lacks engagement with leading academics and industrialists in the field.”

These, says Dr Pike, are the four key facts children should know, but have been distorted or overlooked:

1. Water vapour, not smoke, emerges from cooling towers. These structures are needed whether the heat source is from bio-fuels, concentrated solar rays, coal, gas or nuclear, and are necessary to cool down the circulating vapour (usually steam) that drives the turbines for electricity generation. The heating of water for high-pressure steam to pass through the turbines, followed by condensation, is a fundamental process in the power industry. The use of pictures of cooling towers as ‘iconic’ representations of global warming, therefore, is completely false, as even ‘green’ energy will need these facilities. Additionally, the water vapour emitted from these towers forms part of the natural water cycle.
2. Very low-sulphur fuels can be worse for the environment than higher-sulphur fuels.

Although they are attractive for consuming countries, their manufacture from oil, gas or coal elsewhere is energy-intensive, and therefore globally can leave a larger carbon footprint than conventional higher-sulphur fuels. In the extreme, a tonne of natural gas will produce only half a tonne of liquid fuel, with the remaining half tonne being consumed in the manufacturing process, with associated releases of carbon dioxide. This emphasises the need for full life-cycle analysis of energy processes. This example also illustrates the difficult balance between reducing pollution and acid rain at one location, while adding inadvertently to global warming.

- Oil and other fossil fuels may be burned for another century. Whatever advances are made in renewable and nuclear power, there is likely to be a transition period of at least 100 years during which fossil fuels will continue to be burned globally, driven by the inertia of millions of people depending on their countries' oil, gas and coal production for their own economic prosperity. High priority must be placed on the technologies of carbon dioxide capture and storage, and the coordination of this. Even today, throughout the world, tens of millions of tonnes per day of carbon dioxide would need to be removed from the atmosphere, just to keep the concentration of this gas constant. This puts into perspective the scale of all other activities to reduce global warming. Perversely, even when use of fossil fuels ceases, there could still be further warming. This is because there will be less particulate matter in the atmosphere to reflect sunlight, and a greater proportion of the sun's energy will then reach the Earth's surface.

- Energy storage and transportation (as electricity or hydrogen generated from electricity) will be essential for long-term sustainability. Like many of the energy issues for the future, these will be resolved only through the application of an innovative scientific base in this country, coupled with strong leadership linking education with society's needs, and encouraging constructive engagement amongst all interested parties.

Dr Pike added: "Young people are clearly concerned about global warming and we all have a collective responsibility to ensure that they are well informed and feel confident in challenging the status quo for the benefit of us all."

Dr Janet Moxley's response to Richard Pike's press release

Dr Richard Pike's press release purported to encourage better teaching of the science behind climate change, but itself contained several errors and statements more likely to confuse those being taught about this issue at secondary school level than to give a clear picture of the mechanisms causing climate change and possible mitigation technologies.

The strangest thing about the statement was the items which Dr Pike suggested should be "the four key facts children should know" about climate change. These four facts were (in summary):

- Water vapour, not smoke, emerges from cooling towers.
- Very low-sulphur fuels can be worse for the environment than higher-sulphur fuels.
- Oil and other fossil fuels may be burned for another century.
- Energy storage and transportation (as electricity or hydrogen generated from electricity) will be essential for long-term sustainability.

I would have expected something more along the lines that:

- Climate change is real. (Note 1)
- The climate change is caused by human activities which lead to emissions of greenhouse gases primarily carbon dioxide, methane and nitrous oxide. (Note 2)
- Urgent action is needed to tackle climate change, as 60 – 90% reductions in emissions are needed by 2030 – 2050 if temperatures increases are to be kept to safe levels of no more than 2 °C. Larger temperature increases would lead to positive feedbacks, such as production of greenhouse gases from warming soils and decreased uptake by vegetation reaching the level where climate change continues even without any further anthropogenic emissions. (Note 3)
- No one solution is likely to provide the complete answer. Tackling climate change will need a variety of technologies covering both power generation and energy efficiency, as well as major changes in the behaviour of individuals in the developed world. (Note 4)

Dr Pike has subsequently informed me that he took these points as 'read'. But given the concerns about the quality of science teaching in general, not to mention subsequent reporting of the remarks in the general press, it is unwise to take anything as given and they should be re-iterated firmly before going into any further detail.

Even if my points are taken as 'read', Dr Pike's statement contains some misleading and inaccurate information. Most dangerous is the assertion that oil and other fossil fuels may be burned for another century, as it implies that we can safely sit back and do nothing for another hundred years. Dr Pike's main reason for this is the "inertia of millions of people". While this is indeed a HUGE challenge, it is not an excuse

and every effort must be made by scientists, educators and governments to counter it. After all there was similar public complacency about the health risks of smoking or the unacceptability of drink driving until very recently. People can change their behaviour *en masse* and learn to use new technology in very short periods of time as the growth of internet and email usage over the last 15 years proves.

Dr Pike mentions carbon capture and storage as a possible technology which should be investigated to collect carbon dioxide from fossil fuel burning. While of possible assistance in some cases, this technology is not fully proven and it may be many years before it can play a major role. Where carbon capture and storage has been deployed to date, using the carbon dioxide to extract oil which would not otherwise be economic from depleted reservoirs has been as much of a consideration as preventing greenhouse gas emissions. Thus the benefit of burying the carbon is counteracted by burning the fossil fuel extracted. In any case, carbon capture and storage would not be able to address emissions from diffuse emission sources such as domestic heating systems and transport.

In the same point Dr Pike speculates that reducing the soot emissions associated with burning fossil fuels could accelerate global warming by reducing the amount of sunlight reflected into space. However, this is a complex area which has not been fully modelled. Dark soot such as carbon black which arises from inefficient fossil fuel combustion absorbs sunlight and adds to warming. Only light colour particulates such as nitrate and sulphate reflect it. The effects of particulates are further complicated by their role in cloud formation. Maintaining levels of atmospheric soot is not a valid reason to continue fossil fuel burning.

The other “key facts” also contain worrying inaccuracies and omissions. For example:

1. While it is true that water vapour, not smoke, emerges from cooling towers, this vapour demonstrates the inefficiency of generating electricity from fossil fuels, as it represents a huge amount of waste heat. So cooling towers could

indeed be considered “iconic” of the waste of energy which is leading to global warming.

2. Dr Pike suggests that cooling towers are needed for all forms of energy generation. However, they are certainly not needed for turbines powered by renewables such as hydro, wind, wave or tidal power, or for solar water heating or photovoltaic systems. Nor are they needed when electricity generation is part of CHP schemes.
3. Dr Pike’s discussion of low-sulphur fuels confuses two issues. Low sulphur fuels combat acid rain. But their CO₂ content makes the same contribution to global warming as that in other fuels. Dr Pike implies that we should tackle one problem or the other but not both. However reducing fossil fuel use and vehicle use addresses both problems.

A major concern about the statement was that it gave the impression that it had the support of the 43,000 members of RSC, whereas the press release was essentially Dr Pike’s personal view and was issued without consulting the Society’s Environmental Chemistry Group or, seemingly, other experts within the RSC membership. Dr Pike is entitled to his views, but it would have been probably more prudent to allow expert groups to review his comments. This would add weight to any statement issued.

Few would disagree with Dr Pike’s final statement that “Young people are clearly concerned about global warming and we all have a collective responsibility to ensure that they are well informed and feel confident in challenging the status quo for the benefit of us all”. The RSC has a duty to them to ensure that they are indeed provided with valid information and the scientific literacy needed to make properly informed choices. *Chemistry World* and the *ECG Bulletin* have already carried excellent articles covering this area, but these do not have the impact in the wider world that press releases do, and therefore it is vital that when these are issued on behalf of RSC they are well grounded in established science.

JANET MOXLEY

November 2007

The views in this article are my own, and do not necessarily represent those of my employer, SEPA.

Notes to Dr Moxley’s response

Note 1. ‘Climate change is real.’ S. Solomon *et al* in *Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report on the Intergovernmental Panel on Climate Change*, S. Solomon, D. Qin, M. Manning, Z. Chen, M. Marquis, K. B. Avery, M. Tignor, and H. L. Miller (eds.), Cambridge University Press, Cambridge, UK, Section TS 3.1.1 <http://www.ipcc.ch/>

Note 2. ‘Climate change is caused by human activities which lead to emissions of greenhouse gases primarily carbon dioxide, methane and nitrous oxide.’ S. Solomon *et al*, *ibidem*, Sections TS 2.1.1, TS 2.5, TS 4.1 and Table TS 4.

Note 3. ‘Urgent action is needed to tackle climate change as 60 - 90% reductions in emissions are needed by 2030 - 2050 if temperature are to be kept to safe levels of no more than 2 °C.’

(a) B. Hare, ‘Relationship between Increases in Global Mean Temperature and Impacts on Ecosystems, Food Productions. Water and Socio-Economic Systems’, in *Avoiding Dangerous Climate Change* H. J. Schellnhuber (ed.), Cambridge University Press, Cambridge, 2006, pp 191 – 9.

(b) H. Grassl *et al*, *Climate Protection Strategies for the 21st Century; Kyoto and Beyond*, Wissenschaftliche Beirat des Bundesregierung Globale Umweltveränderung (German Advisory Council on Global Change) Special Report, Berlin, 2003.

(c) European Council target limit on global temperature increase: CEU—Council of the European Union (1996), 1939th Council Meeting, Luxembourg, 25 June 1996. For a comment on this policy, see R. S. J. Tol, ‘Europe’s long-term climate target. A critical evaluation’, *Energy Policy*, 2007, **35**, 424-432.

Note 4. ‘No one solution is likely to provide the answer.’

(a) *Climate Change the UK Programme 2006*, HM Government, 2006 (pdf version available on the web).

(b) *Inquiry into Energy Issues in Scotland*, Royal Society of Edinburgh, 2006 (pdf version available on the web).

(c) *Changing Our Ways: Scotland's Climate Change Programme*, Scottish Executive, Edinburgh, 2006 (pdf version available on the web).

(d) George Monbiot, *Heat: How We Can Stop the Planet Burning*, Penguin Paperback, 2007.

(e) Dave Reay, *Climate Change Begins at Home*, Macmillan Science, 2005.

Biographical Note: Janet Moxley is an environmental chemist who works for the Scottish Environment Protection Agency (SEPA). Dr Moxley's interest in the chemistry associated with climate change arises from studying for a PhD with Keith Smith's group at Edinburgh University. For her PhD, Janet investigated carbon monoxide exchanges between soils and the atmosphere. Carbon monoxide affects the sink for greenhouse gases such as methane and nitrous oxide, which also have sources and sinks in soils. Prior to her PhD research, Janet obtained a BSc in Chemistry, and an MSc in Analytical Chemistry from Aberdeen University.

Dr Richard Pike's reply

I am delighted to have the opportunity to respond to Dr Janet Moxley's commentary on my press release. Whilst we might disagree on the emphasis on the future make-up of the world's energy supply, there is no disagreement over the seriousness of the climate change threat we face or the need to react positively and directly to address these critical issues.

The major criticism in the comment piece is really about the issue of media releases. Media releases can be powerful tools in shaping debates, and the RSC has been successful in recent years in setting the agenda in the media in several areas using this form of communication. Media releases have to be used with care because they are not, and cannot be, 'balanced' articles. Media releases are most effective and have greatest impact when the points made are incisive and challenging, either setting the agenda on a topic or responding to a specific issue. Taken out of context, media releases may appear as 'incomplete stories' or even 'one-sided'.

The media release cited above was in response to a specific story about science teaching on climate change. It built upon what is taught but also sought to highlight some of the other

issues that need to be addressed. The points raised are scientifically consistent and the positions stated draw upon the RSC policy position. All media statements are carefully checked before they are issued for alignment with RSC policies.

I'm sorry if what I have said has caused concern. I and my colleagues on the staff see our role as promoting good debate on science issues. I'd welcome the opportunity to come to one of your meetings to discuss these issues with you. By open debate we could explore how to develop new channels to help move the public's need to address the issue of global warming and climate change.

RICHARD PIKE

December 2007



Meeting report

RSC Gas Kinetics Discussion Group Meeting in honour of Professor Mike Pilling

On the 9th and 10th of September 2007 the Royal Society of Chemistry Gas Kinetics Discussion Group held its summer meeting at Devonshire Hall, University of Leeds. The meeting celebrated the life and work of **Professor Mike Pilling** – particularly his contributions to developing the synergies and symbioses that result from combining field data, laboratory results, and theoretical approaches to the understanding of atmospheric chemistry.

The **first session**. (The Pilling legacy) was chaired by **John Plane** (Leeds) and commenced with a paper by **Mark Brouard** (Oxford) on his use of "Quantum beat spectroscopy as a probe of angular momentum polarization in chemical processes". Collisional depolarisation cross-sections for OH and NO were measured using both Zeeman and hyperfine quantum beat spectroscopy.

The second paper ("Steady state master equation (SSME) methods for multiple well systems" – **Nicholas Green**,

Oxford) extended the application of SSME methods to low temperature processes and to the relationship of the ensemble of contributory rate constants to the overall rate of systems such as the multiple well isomerisation reactions of allene-cyclopropene-propyne (a 3-well system).

Roberto Sommariva (NOAA) spoke about urban plume reactions and the formation of secondary organic compounds from VOCs in the North East US ("Secondary organic chemistry in an urban plume"). Using a model

based on the Leeds Master Chemical Mechanism and data from NOAA WP-3D aircraft sampling (2004), the formation of nitrates (C2-C5) – including PAN – and carbonyls (C3-C5) were studied in a plume over New York by GC-MS and PTR-MS detection. The work extends the understanding of urban plume reactions and their role in urban fallout pollution effects. Further field work (Mexico City, Houston) and adaptations of the Photochemical Trajectory Model are planned.

Manik Pradhan (Bristol) reported on the development of a variety of cavity enhanced detection methods for monitoring a range of atmospheric components (“Application of cavity enhanced spectroscopy methods in atmospheric chemistry”). Long path lengths of multiply reflected light in the instrument cavity produce high detection sensitivity in the atmosphere (ppb(v) or ppt(v)). For instance, the atmospheric concentration of C_2H_2 (0.8 – 2.5 ppb(v)) was measured using a pre-concentrating/purifying trap to remove other gases and to reduce the pressure (and hence pressure broadening of the detection signal). IO radicals (an important species for Marine Boundary Layer aerosol formation) were also examined.

A paper by **Ian Smith** (Cambridge) opened the **second session** (chaired by **Robin Walsh** (Reading)) – “Understanding reactivity at very low temperatures: the reactions of $O(^3P)$ with alkenes.” Neutral-neutral reactions were studied via the $O(^3P)$ + alkene system (ethene, propene, butene) at temperatures down to 25 K using isentropic expansion of gas through a Laval nozzle. These are important processes for the chemistry of dense interstellar clouds where very low temperatures (~13 K) occur. Semi-empirical predictions and theoretical estimates were compared with experimental data with excellent agreement (*Science*, 2007, **317**, 102).

Arkke Eskola (Helsinki) then described his work on chlorine-radical reactions (“Kinetics of reactions of several alkyl radicals with Cl_2 in the temperature range 190-360 K”). A new rate constant for the $C_2H_5\cdot + Cl_2$ reaction was obtained which was significantly higher than that obtained

previously. This work has been published recently in the *International Journal of Chemical Kinetics*, 2007, **39**, 614-619.

“Infrared spectroscopic study of the effect of oleic acid on the deliquescence behaviour of ammonium sulphate aerosol particles” by **Juan Nájera** (Manchester) investigated the effect of the common particle constituent oleic acid on the deliquescence phase transition of $(NH_4)_2SO_4$ particles using a room temperature aerosol flow tube, FTIR detection, and SEM/EDX for particle morphology and chemical composition studies. The deliquescence relative humidity showed little dependence on the amounts of oleic acid present (‘slightly lowered or not affected’) which is consistent with earlier studies of the effects of water insoluble fatty acid coatings on such phase transitions.

The final paper in the second session (“Experimental and theoretical study of the $HO_2 + SO$ and $HO_2 + SOCl$ reactions”) came from **Christa Fittschen** (Lille) who talked about the experimental aspects and **Bela Viskolcz** (Szeged) who talked about the theoretical aspects. Their work described how although $SOCl_2$ photolysis in the presence of methanol and oxygen was used to generate HO_2 , the reactions of SO and $SOCl_2$ in this system are not well understood and so further investigation of the $SOCl_2/CH_3OH/O_2$ photolysis system were undertaken using a combination of laser flash photolysis and continuous wave cavity ring down spectroscopy. The HO_2 decay did not obey second order decay kinetics and HO_2 and $SOCl$ were shown to form the adduct $HOOSOCl$ (which dissociates to OH and $ClSO_2$) whilst $SO + HO_2$ decayed to give $HOOSO$ which (by O-O bond breaking) gave OH and SO_2 . The $SOCl + HO_2$ reaction was then examined using a variety of quantum methods. A van der Waals complex was identified as a possible precursor to the $HOOSOCl$ adduct and the subsequent decay (to $OH + ClSO_2$ followed by decay to $OH + SO_2 + Cl$) was demonstrated to be energetically preferred. Hydroxyl concentrations can reach 10% of those of HO_2 and its formation is consistent with the observed deviation of the HO_2 profile from second order behaviour.

Tuesday’s session (**Session 3**: Synergies between experiment and theory) was chaired by **Struan Robertson** (Leeds) and commenced with **Stephen Klippenstein** (Argonne) surveying “Synergies between theory and experiment for radical reactions.” Methyl radical recombination, hydroxyl + ethylene, and hydroxyl + methyl radical were discussed as representative of systems for which the availability of experimental data over extended ranges of temperature and pressures provided a stimulus for extensions of theoretical approaches based around transition state theory (e.g. direct variable reaction co-ordinate transition state theory; VRC-TST). The paper was not only a fine example of the synergy between new experimental data and the theoretical responses they produce but also a clear demonstration of the value of Kuhnian approaches to scientific research.

Marie Thérèse Rayez (Bordeaux) presented a paper on “Experimental and theoretical study of the water vapor effect on the nitric acid formation in the $HO_2 + NO$ reaction”, which focused on the minor channel for HO_2 and NO (i.e. $HO_2 + NO \rightarrow HNO_3$) – as opposed to the major channel (i.e. $HO_2 + NO \rightarrow OH + NO_2$). A full range of pressures and temperatures appropriate to the troposphere were used in the turbulent flow reactor with CIMS analysis. The presence of water vapour increased nitric acid formation; this observation was supported by the theoretical calculations which showed that H_2O reduced the barrier for isomerisation of the $HOONO$ complex (formed first from $HO_2 + NO$) to nitric acid.

Gabriel Balint-Kurti (Bristol, “Ketene photolysis: The statistical adiabatic product distribution (SAPD) approach to the calculation of the final quantum state distributions and Total Kinetic Energy Release Spectra”) talked on unimolecular dissociation processes with particular reference to highly excited singlet ketene and the use of adapted variational RRKM (or microcanonical transformation state theory) treatments to predict the quantum states and the relative kinetic energy distributions of the products from its dissociation.

The final paper of Section 3 (“The reaction of the hydroxyl radical with acetic acid”) from **Vung Bui** (Leuven) noted that even though the major gas phase sink for acetic acid in the upper troposphere was by reaction with OH, issues exist around the product distribution (i.e. the balance between H-abstraction of the acidic-H or the methyl-H) and around the interpretation of the observed negative T dependence on the unusually large low temperature rate constant effects (which shows a strong positive T dependence at T>500K). The work showed that the formation of pre-reactive complexes followed by H-atom tunnelling accounted for the rate constant effects of temperature and a swap from acidic-H abstraction as the dominant processes to direct abstraction from the methyl group was predicted at higher temperatures.

Session Four (Chair: **Ian Sims** (Rennes)) began with a presentation from **Mike Nicovich** (Atlanta) about the “Kinetics, mechanism and thermochemistry of the gas-phase reaction of atomic chlorine with pyridine”. Emissions of pyridine into the atmosphere are from industrial activity and coal combustion and it has a role in the atmospheric ion chemistry (particularly ion-induced nucleation of atmospheric particles); primary atmospheric sinks are reactions with OH and HNO₃. Pyridine-atomic chlorine reactions may also be important for marine and coastal atmospheric chemistry and the reported work used laser flash photolysis and atomic resonance fluorescence spectroscopy to study $\text{Cl} + \text{C}_5\text{H}_5\text{N} \rightarrow \text{o-C}_5\text{H}_4\text{N} + \text{HCl}$ (hydrogen abstraction), $\text{Cl} + \text{C}_5\text{H}_5\text{N} + \text{M} \rightarrow \text{C}_5\text{H}_5\text{N-Cl} + \text{M}$ (adduct formation) and $\text{C}_5\text{H}_5\text{N-Cl} + \text{M} \rightarrow \text{Cl} + \text{C}_5\text{H}_5\text{N} + \text{M}$ (adduct dissociation).

The increased interest in biofuels reflects concerns about energy security (the US has moved from being self-sufficient to a 70% dependence on imported fuel) and climate change (George Bush has targeted 35 billion gallons of alternative fuel for 2017) – though in general biofuels are more expensive than fossil fuels. **Tim Wallington** (Ford Motor Company) examined some of the chemistry of biofuels (“Atmospheric chemistry of automotive biofuels: insights from

theory and experiments”). The methyl esters of long chain fatty acids (e.g. palmitic, stearic) are used for blending in diesel and alcohols (Ethyl, Propyl, Butyl) are used in gasoline. Using FTIR smog chamber techniques and *ab initio* calculations the kinetics of Cl atom oxidation in alcohols (isopropanol + Cl in the absence of oxygen) were examined and Tim Wallington discussed these findings in relation to the environmental impact of automotive biofuels.

Anthony Hynes (Miami) spoke on “Experimental and theoretical studies of the reaction of the OH radical with alkyl sulfides”. Interest in this field has been stimulated by the importance of DMS and OH reactions as sources of SO₂ and the consequent formation of condensation nuclei at the MBL. The experimental system (pulsed laser photolysis (H₂O₂ to get OH) pulsed laser induced fluorescence) gave data on the rate constants for the formation and dissociation of OHDMS, OHMES and OHDES over 50-650 Torr and at 240-245 K in the presence of O₂ and electronic structures were calculated for OH-alkyl sulfide adduct formation showing bound structures consistent with the experimental observations.

Craig Taatjes (Sandia) closed Session Four by describing how the combination of multiplexed MS with photoionisation by tunable synchrotron radiation provides a powerful experimental tool for elementary reaction kinetics (“Imaging combustion chemistry by multiplexed synchrotron photoionization mass spectroscopy”). The Advanced Light Source at Lawrence Berkeley National Laboratory was used as a tunable-energy photoionisation source to study the detail of flame chemistry as a function of position in the flame. Changes in the PIE (Photoionisation Efficiency) of the reacting mass (the flame) with time after photolysis gives data on time-resolved isomeric compositions in reacting systems which can help “reveal the mechanisms of key reaction pathways in hydrocarbon ignition”. These studies are important in pollution control (e.g. soot formation) and in non-linear feedback systems such as in ignition chemistry (alkyl and O₂ systems) in combustion/compression engines.

The **final session** (Kinetics in field measurements and modelling) was chaired by **Bill Bloss** (Birmingham). **Dwayne Heard** (Leeds) spoke on “Kinetics and field-measurements of free-radicals in the atmosphere: a symbiotic relationship” and described field measurements of free-radicals which stimulated laboratory studies (and *vice versa*) in particular O(¹D) + N₂; ClO + ClO ↔ Cl₂O₂; photolysis yields from CH₃CHO and near-IR photolysis of HO₂NO₂ were discussed. (1) O(¹D) + N₂ → O(³P) + N₂. New rate constant (20% above recommended) meant modelled values for OH were reduced by 10% in close agreement with measurements. (2) Acetone photolysis is also an important OH source – with marked wavelength (quantum yield) and temperature dependence – using recent experimental data the new production rate for HOx in the upper atmosphere is three times lower than the previous values calculated. (3) Results from twilight measurements of HO₂NO₂ in the stratosphere by balloon initiated laboratory based studies of UV and IR cross-sections which identified a previously unrecognised acetone dissociation of the HO₂NO₂. (4) Photolysis of ClOOCl is the rate determining step in the loss of polar ozone, i.e. Cl + O₃ → ClO + O₂; ClO + ClO + M → ClOOCl + M; ClOOCl + hv → Cl + ClOO. Hence the rates of the reactions in the mechanism are important for understanding polar ozone loss. A new cross-section much lower than previous values has been generated and this has caused a re-evaluation of previous understanding.

Nicola Carslaw (York, “What have we learnt by comparing modelled and measured OH?”) compared hydroxyl data from large field campaigns; early campaigns were carried out with novel instruments and tended to be sporadic. This has improved from one day of modelled and measured OH being compared in 1996 to 8 days in 1997. Results suggested uncertainties in heterogeneous HO₂ loss and the nature of the VOCs present – and more campaigns were undertaken which resolved these unknowns. Hand-in-hand with extensions in field measurements, laboratory-based studies by kineticists also helped resolve uncertainties (e.g. O(¹D) with N₂ was redetermined). The TORCH campaign

(2003/2004) was “the most highly instrumented campaign to date in the UK”. Fifty-two gas phase as well as aerosol values, meteorological parameters etc. were measured over a 33-day period. This extensive dataset once again showed significant disagreement between measured and modelled radical concentrations for as yet unknown reasons. The roles of acetone (the concentration is important for measured OH but not so important for modelled OH) and of other species (e.g. isoprene) are revealed by differences between field data and modelling results. This allows effort to be focussed on these key causes of differences between monitoring and modelling.

Much isoprene was observed (100 ppt), little NO (20 ppt), surprisingly large amounts of OH (many times larger than could be simulated by models). The difference was associated with the isoprene degradation mechanism which was based on an $\text{HO}_2 + \text{CH}_3\text{C}(\text{O})\text{O}_2$ termination reaction. A laboratory-based re-investigation using pulsed laser peroxy radical generation and OH detection by pulsed laser induced fluorescence showed significant non-terminating OH production from the reaction ($\rightarrow \text{O}_2 + \text{HO} + \text{CH}_3\text{C}(\text{O})\text{O}$) which data is now being used to remodel the model over the Amazonian rain forest.

Terry Dillon (Max Planck, Mainz) spoke about the effect of tropical ecosystems the atmospheric oxidation capacity and the Earth’s climate on HOx concentrations and the GABRIEL (Guyanas Atmosphere-Biosphere Exchange and Radicals Intensive Experiment with the Learjet) campaign to observe HOx over the Amazon (HOx recycling via the reactions of peroxy radicals – interpretation of field measurements over the rainforest).

Rachel Porter (Reading) then talked on “The gas-phase ozonolysis reaction of cyclohexene” in which she described the use of cyclohexene as a model compound (analogous to the endocyclic terpenes, e.g. α -pinene) to investigate the role of terpene ozonolysis reactions as a source of global secondary organic aerosol. Hydroxyl scavengers (cyclopentane and ethanol) were used to ensure that only ozone-cyclohexene

reactions occurred (95% of OH scavenged). An eighty litre chamber (cyclohexene 25 ppmv, Ozone 2-20 ppmv, large excess of hydroxyl scavenger), particle phase sampling onto membrane filters, GC/MS, GC/FID were used to identify reagents and gas-phase products. Data were in agreement with proposed mechanisms (based on the Criegee ozonolysis mechanism) which was used in numerical kinetic simulation and compared to laboratory findings.

Joanna Barnes (Cornwall) discussed the use of small area nitrogen dioxide measurements (diffusion tubes) with traffic, altitude and land data in a GIS-based approach to make predictive evaluations of the pollution effects of traffic in rural towns with canyon streets. This low-cost, semi-empirical predictive technique gave good agreement with independently measured nitrogen dioxide concentrations and did so with higher accuracy than most alternative desk-based models recommended by central government (“GIS-Based Techniques for Predicting Traffic Pollutants in Cornwall”).

Sandra Saunders (University of Western Australia) discussed the secondary organic products generated by refinery emissions (Alcoa Wagerup) using monitoring data and chemical kinetic models (“Photo-oxidation from well-defined refinery sources: Measurements, modelling and further developing of the Master Chemical Mechanism”). The refinery was isolated and had a good time series record of emissions (14 VOCs); it was therefore a good test bed for the research. Extensive additional monitoring was also undertaken. The work is continuing to extend the model, increase its accuracy and work with Alcoa to use it for environmental benefit. Twenty-five species (including acrolein – a highly reactive VOC) were present, 20 are already part of the MCM, 5 new VOCs (e.g. acrolein, vinyl chloride, butenal) are being introduced and it is hoped that a refinery stack emissions model will be created (with a 250 km² background airshed model).

Alastair Lewis (York) closed the final session of the conference with a paper on the “Chemistry of the tropical North

Atlantic boundary layer”. He pointed out that long-range transport across the North Atlantic set baseline values for species such as O₃ and CO. However, some of the North Atlantic air from continental North America is drawn to the Equator (Azores high pressure system) and the chemical fate of such air is uncertain for these systems. The work reported the first set of chemical measurements in the Tropical Eastern North Atlantic (São Vicente) – ozone destruction was observed (2-10 ppbv d⁻¹), and although [NO] has less than 10 pptv its concentration (which is air mass dependent) determines ozone loss. Similar losses were observed from aircraft throughout the Marine Boundary Layer (~800 m) and in the overlying free troposphere (2500 m). The remote Tropical North Atlantic boundary layer may therefore be a sink to around 50-100 Tg ozone per year (mostly of mid-latitude origin).

Although the talks presented at this meeting were a draw in themselves, the majority of speakers and delegates had come to celebrate a career shared with their colleague, supervisor, collaborator and friend, **Professor Mike Pilling**. Mike has enjoyed a long and illustrious career researching and publishing in the field of atmospheric chemistry, combustion, interstellar chemistry, chemical kinetics, laser flash photolysis and modelling elementary reactions and complex reactions. Mike will be sadly missed from the field, although I suspect he may remain a notable figure on the conference circuit. Good luck, Mike!

Dr LEO SALTER
Cornwall College,
Pool, Redruth, Cornwall
leo.salter@cornwall.ac.uk



Professor Mike Pilling

Forthcoming symposium

The science of carbon trading

Royal Society of Chemistry Environmental Chemistry Group

2008 Distinguished Guest Lecture & Symposium

A **one-day** meeting to be held in the Council Room of the Royal Society of Chemistry, Burlington House, Piccadilly on Wednesday, 12th March 2008, from 10:30 am onwards.

The **2008 ECG Distinguished Guest Lecturer** will be **Dr Terry Barker**, Director, Cambridge Centre for Climate Change Mitigation Research (4CMR)

Symposium & Distinguished Guest Lecture

The Science of Carbon Trading

PROGRAMME

10:30 Coffee/tea and registration
11:00 Chairman's Introduction, Dr Brendan Keely (Chairman, ECG)

11:05 Professor Jon Lovett (University of York) *Having our climate cake and eating it: Reduced Emissions from Deforestation and Degradation*

11:45 Matthew Owen (Cornwall College) *REDD Bull: What can rainforest protection do to halt climate change?"*

12:30 **Environmental Chemistry Group 35th Annual General Meeting** and lunch

13:15 Dr Ausilio Bauen (Imperial College, London) *Ensuring a future for low carbon sustainable biofuels*

14:00 Miles Austin (EcoSecurities) *How a cold snap in Kent raises the Karachi Carbon price*

14:45 Coffee/tea

15:00 Introduction to the 2008 ECG Distinguished Guest Lecture and presentation of the ECG DGL Medal

15:05 **RSC Environmental Chemistry Group Distinguished Guest Lecture for 2008:** Dr Terry Barker, (Cambridge Centre for Climate Change Mitigation Research) *Achieving the EU 2 °C target through carbon trading*

16:05 Open Forum

16:30 Close



Venue: Royal Society of Chemistry, **Burlington House**, Piccadilly, London, W1J 0BA

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. Guests are welcome and an amount of £40 is payable for non-members of the ECG (£25 concessions). 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-fifth Annual General Meeting, 12 March 2008 and Distinguished Guest Lecture & Symposium on *The Science of Carbon Trading*

Please tick the item(s) below as appropriate, I would like to attend:

The AGM The Symposium

I enclose a cheque for:

£25 registration fee (ECG members/non-ECG concessions) RSC membership no. _____

£40 registration fee (non-members of the ECG)

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

Name:

Address:

Email:

Please send to: Dr Leo Salter, Opie, Cornwall College, Pool, Redruth, Cornwall TR15 3RD leo.salter@cornwall.ac.uk
Fax 01209 611632

Royal Society of Chemistry Environmental Chemistry Group

2008 Distinguished Guest Lecture & Symposium

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Abstracts and biographical details of the speakers

Having our climate cake and eating it: Reduced Emissions from Deforestation and Degradation

Professor Jon Lovett,
University of York

Is it possible to reduce greenhouse gases, alleviate poverty and save biodiversity all in a single policy instrument? Potentially yes, if the debates on Reduced Emissions from Deforestation and Degradation (REDD) become reality. The principle is very simple. Woody plants fix CO₂ through photosynthesis but much land-use in the tropics causes loss of woody vegetation. The Intergovernmental Panel on Climate Change (IPCC) estimates that 20-25% of current annual carbon emissions result from loss of tropical forest, though this is a major underestimate as it does not take degradation of dry forests into account. If that process can be reversed then huge amounts of carbon can be fixed with very little cost or effort. The numbers are compelling. Margaret Skutsch and members of the Kyoto: Think Global, Act Local project at the University of Twente estimated the degradation off-take figures for tropical dry forest, which is the best vegetation type to achieve poverty alleviation objectives, for seven southern and eastern African countries to be around 178 m tons/year. The opportunity costs, in other words the payments needed, to prevent this degradation would be between \$0.8 and \$5.2 per hectare per year depending of the level of off-take or \$0.7- \$1.8 per ton of CO₂.

Compensation payments for dry forest conservation by local communities through Kyoto mechanisms would thus enable sustainable forest management, continued extraction of local forest products and biodiversity conservation in return for reduced degradation.

Jon Lovett is professor of Sustainable Development in the Technology and Sustainable Development group at the University of Twente in the Netherlands and Director of the Centre for Ecology, Law and Policy at the University of York, England. He was on the Programme Advisory Committee for the Natural Resources Systems Programme of the UK Department for International Development (1999-2006) and Senior Advisor to the Lower Kihansi Hydropower Environmental Monitoring and Catchment Management Projects, Tanzania (1996-2002). From 1996 to 1997 he was on the joint Economic and Social Science Research Council and Natural Environment Research Council committee on environmental economics and was responsible for preparing the policy report reviewing provision of advanced courses in environmental economics, environmental evaluation and risk assessment. He has spent more than 12 years living and working in developing countries on a wide range of projects and has published extensively on natural resource management. His current research is focused on the broader implications of climate change, including the impacts of a shift to biofuels; and the institutional economics of decentralised community management of forests.

REDD Bull: What can rainforest protection do to halt climate change?

Matthew Owen, Cornwall College

Reduced emissions from deforestation and degradation (REDD) are potentially one of the cheapest and most effective means of setting global emissions on a path that would contain surface warming to 2 °C. Nonetheless, existing carbon market structures are inadequate if the scale and speed of investment required is to be delivered. Following

the Bali conference, a path to integrating REDD into future carbon markets is still unclear with a number of competing options. Ring-fencing funds for avoided deforestation projects or relegating derived carbon assets to the voluntary market will achieve nothing more than a series of sub-scale and unsustainable pilots. Instead, credits through reduced deforestation should be fully integrated into the global carbon market no later than 2012. Carbon price stability should be achieved by allocation of Assigned Amount Units (AAUs) to rainforest nations to ensure the global cap increases at the same rate as the supply of carbon assets.

Matthew Owen is head of research at the Cornwall Business School (CBS), part of Cornwall College where his research interests include carbon finance and environmental resource trading. He is also directing the Eliasch review into Financing Mechanisms for Avoided Deforestation and Clean Energy commissioned by the Prime Minister in September 2007. Matthew is also Acting Director of Cool Earth, a UK-based organisation that is pioneering avoided deforestation as a credible means of tackling climate change. Cool Earth Action is a registered charity, launched in June 2007 with the backing of Sir David Attenborough and Sir Nicholas Stern. It has 14,000 members in 14 countries and has secured over twelve million tonnes of CO₂ in 36,000 individually sponsored acres of endangered rainforest. Prior to joining Cornwall College, Matthew was a director with Morgan Stanley. He is married to the artist Hannah Woodman and has three daughters.

Ensuring a future for low carbon sustainable biofuels

Dr Ausilio Bauen, Imperial College, London

Ausilio Bauen is Head of the Bioenergy Group at the Centre for Energy Policy and Technology at Imperial College London, and Director of E4tech, a strategic and techno-economic consultancy focused on

sustainable energy. He graduated in physics engineering at the Swiss Federal Institute of Technology in Lausanne and holds MSc and PhD degrees in energy technology and policy from Imperial College and King's College in London. He has considerable research and consulting experience in new and renewable fuels and technologies for stationary and transport applications, and has worked with private and public sector organisations to develop and implement sustainable energy strategies. He has acted as an advisor to the EC's Biofuels Technology Platform, Alternative Fuels Working Group, High Level Group on Hydrogen and Fuel Cells, and Climate Change Programme, and to the UK's Energy Review, Stern Review, Chief Scientist, Royal Commission on Environmental Pollution, and Low Carbon Vehicle Partnership. He is also a member of the GEF Science and Technology Advisory Panel roster of experts. He has led the development of the RTFO's Carbon Reporting scheme.

How a cold snap in Kent raises the Karachi Carbon price

How the Kyoto Protocol's Flexible trading mechanisms and the European Union's Emissions Trading Scheme (EU ETS) interact today and how this could develop post-2012

Miles Austin, EcoSecurities

The EU ETS has been operating since 2005. The scheme primarily takes in heavy industry from the power and heat, iron and steel, glass and ceramics, pulp and paper, refinery and cement sectors, currently covering 46% of the EU's emissions. The Kyoto Protocol has three flexible trading mechanisms designed to increase abatement opportunities and decrease cost to participants. The two project based mechanisms are the Clean Development Mechanism (CDM) and Joint implementation (JI). Of these the CDM has been the dominant partner with some 2.2 Billion tonnes of CO₂ reductions scheduled to be carried out to 2012. From early on in its inception a link from the EU ETS to the Kyoto protocols flexible trading mechanisms was envisaged in order to allow European Industry access to abatement opportunities outside of the EU and to help guide the rapid industrialisation of the developing world down a lower carbon path. The link has a number of

implications for both Europe and CDM host countries. For instance European weather now influences the Carbon price in Brazil. How and why such effects occur will be the focus of the lecture.

Miles Austin works in Oxford as EcoSecurities' Senior Carbon Market Analyst within the Commercialisation team, which focuses on managing transactions of the Group's carbon credit portfolio and identifying potential credit buyers. Miles' responsibilities include monitoring market and policy developments, analyzing scenarios and developing strategies. Previously Miles worked in EcoSecurities Global Consulting Services team, based in The Hague, where his roles ranged from providing guidance to new entrants to the EU Emissions Trading Scheme (ETS), preparing Clean Development Mechanism (CDM) Project Design Documents (PDDs), and market analysis. Miles' involvement in the field of carbon trading began in 2004, with the Environmental Technology MSc at Imperial College, specialising in climate change and policy. He completed the course with a research internship at Point Carbon in Oslo, looking at the Kyoto policies of the EU15 Canada and Japan, in order to estimate the final Kyoto Gap. Subsequently, Miles worked as an analyst for Point Carbon in the Research and Advisory team, researching companies' actions and strategies in relation to the EU ETS. Miles sits on the Carbon Markets Association executive and chairs the CDM working stream. He additionally acts as the second for Dr Pedro Moura Costa, Chair of the Environmental Industries Commission's Carbon Trading Working Group.

Achieving the EU 2 °C target through carbon trading

Dr Terry Barker, Cambridge Centre for Climate Change Mitigation Research

The carbon market is a market in financial instruments, giving rights to emit carbon dioxide into the atmosphere, (the "allowances" of the European Union's Emission Trading Scheme – the EU ETS) subject to legal restrictions as to their use. It is a

market created by governments to manage the climate-change externality in a market system. The lecture will consider such markets in the context of avoiding dangerous climate change and in terms of institutional theory and the experience of the EU ETS. The objective of carbon trading is to provide market signals and incentives to stimulate low-carbon products and processes, and more importantly technological innovation, at lowest costs. The lecture will cover the extension of the market to other regions, sectors and gases, as well as problems such as potential price instability, risks of market collapse (as in Phase 1 of the EU ETS), unacceptable costs, and limits to trading, including the conditions in which carbon taxation may be preferable. Some observations will be made on the carbon prices likely to emerge from global carbon trading that will lead to widespread adoption of carbon capture and storage and other technologies required for the EU 2 °C target increase in global average temperatures above pre-industrial to be achieved.

Terry Barker is Director of the Cambridge Centre for Climate Change Mitigation Research (4CMR), Department of Land Economy, University of Cambridge, and Leader of the Tyndall Centre's Integrated Modelling programme of research and Chairman of Cambridge Econometrics. He was a Coordinating Lead Author in the IPCC Third Assessment Report, 2001, for the chapter covering mitigation and the world energy industries. He is a Coordinating Lead Author in the Fourth Assessment Report, 2007, for the chapter on mitigation from a cross-sectoral perspective, covering the macroeconomic costs of mitigation at national, regional and global levels in the short and medium term (to 2030). Research interests are in greenhouse gas mitigation policy, large-scale computable energy-environment-economy and world energy modelling. He has directed and co-ordinated many large projects building and applying large-scale economic models of the UK, the European Union and the global economy. See <http://www.landecon.cam.ac.uk/4CMR/4CMR.htm>.



MRC Integrative-Toxicology Training Partnership (ITTP)

Call for Applications

The MRC is launching a new initiative aimed at improving and securing capacity in the toxicological sciences. Through partnerships between academia, industry and government the initiative will seek to build the expertise in toxicology and related disciplines that is required to ensure the safe and effective development of drugs, chemicals and consumer products, and to provide better assessment of risk deriving from environmental exposure.

The MRC-ITTP will run an annual competition to support PhD studentships and Career Development Fellowships in Toxicology. The emphasis will be on aligning modern cell and molecular biology with other fundamental and health-related disciplines relevant to Toxicology to provide an integrated approach to research and training in the toxicological sciences.

The ITTP will be managed by the MRC Toxicology Unit at the University of Leicester.

ITTP PhD Studentship Scheme

Applications are sought for 4-year PhD studentships for training in the toxicological sciences.

The studentships are intended to encourage the application of cutting edge science and technology to

toxicology, and to provide opportunities for a thorough training in all aspects of the discipline. Research projects should meet the main aim of ITTP in achieving cross-fertilisation between toxicology and advances in other disciplines.

A key feature of the initiative will be its training programme which will bring together aspects of established toxicology courses with an annual residential academy designed exclusively for ITTP PhD students and Fellows. Students will also benefit from a broad training in generic and transferable research and scientific skills.

Applications may be from a single academic institute, from two or more academic units, or from a collaboration of academia with a relevant government agency, or with an industrial laboratory. In cases of collaborative applications it will be necessary to display clearly the contributions of each partner.

ITTP Career Development Fellowships (CDFs)

The CDFs are intended to attract applications from experienced postdoctoral fellows (3-10 years after a Ph.D. or MD degree) who wish to conduct research within the broad framework of toxicology and consistent with the aims of the ITTP. Applications are encouraged from scientists who have trained in other disciplines and who now wish

to apply their skills and expertise to the toxicological sciences. Fellowships will be of 3 years duration. Priority will be given to applications that incorporate collaborative research. The ITTP will provide competitive salaries and bench fees.

Funding available

MRC has allocated a minimum £2.25M for this initiative. Funding for up to 6 Research (PhD/DPhil) Capacity Building Studentships and 2 Fellowships is available for 2008 and will be followed by further annual calls for proposals.

Assessment criteria

Applications will be assessed by a Scientific Committee [1] established by the programme Steering Committee [2]. Decisions will be reached on the basis of scientific quality, feasibility, the integrative nature of proposed projects in line with the aims of the call and the likelihood of success. Key criteria for assessment will be:

- The novelty of the research proposal in the field of toxicology.
- The relevance of the proposal in the light of present toxicological concerns for human health.
- Proposals that span and use a variety of skills in both in vivo and in vitro contexts.

- For PhD Studentships the likelihood of the applicant providing the appropriate scientific environment and guidance to students.
- For CDFs the track record of the applicant in innovative research.

How to apply

Application forms for PhD studentships can be downloaded from the MRC Toxicology website, under the heading Integrated Toxicology Training Partnership <http://www.le.ac.uk/mrctox/MRCTox/ittp.htm>.

After completion application forms should be sent to Dr Andy Smith ags5@le.ac.uk.

For CDFs, potential applicants should contact Dr Andy Smith, by Email or by telephone 0116 252 5617, in the first instance.

Deadline dates

Deadline for receipt of applications for PhD Studentships is 31st January 2008.

Peer review of applications will be in February 2008.

Funding decisions to applicants are to be made by the middle of March 2008.

Deadline for receipt of applications for Career Development Fellowships is 31st March 2008.

Please note that applications received by the MRC after the deadline stated or outside the remit

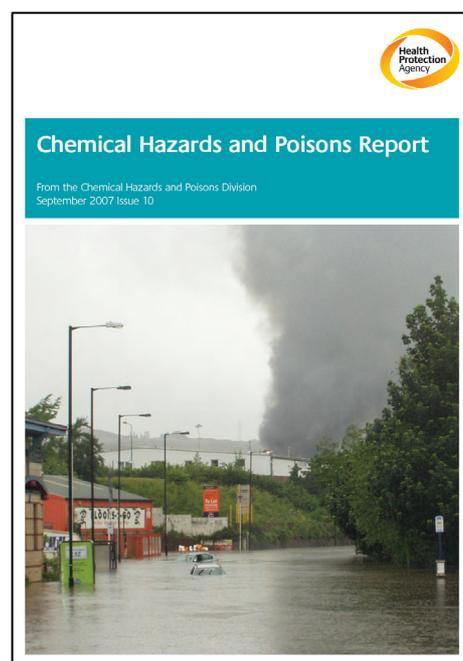
of the call will be rejected. There will be no scope for applicants to respond to reviewers' comments. The decision of the scientific committee will not be open to appeal.

Contact and guidance

If you have any queries on your proposal please email: ags5@le.ac.uk or lsj2@le.ac.uk.

[1]The membership of the Scientific Committee will be published shortly.

[2]The ITTP Steering Committee consists of Prof. P. Nicotera (Chairman), Prof. K. Chipman, Prof. P. Elliott, Prof. S. Holgate, Dr C. Joseph, Prof. I. Kimber, Prof. P. Matthews, Dr R. Peck, Dr L. Smith and Prof. K. Woods.



Health Protection Agency Chemical Hazards and Poisons Report (September 2007)

The latest *Chemical Hazards and Poisons Report* (September 2007) is now available from the Health Protection Agency web site: www.hpa.org.uk/

The articles include incident responses to flooding, fireworks, phosphorus grenades, and remediation of contaminated land, plus the usual round-up of conferences and training events.

There is a feature on 'Odour Issues', and another on emergency preparedness, which includes an item about the Chemical Exposure Assessment Kit (ChEAK), developed by the HPA in consultation with the Laboratory Review and Liaison Group. This group consists of national experts in biomonitoring and includes Kate Jones, the OETG Secretary, who represents the Health & Safety Laboratory.

As well as defining the kit, the group are producing guidance and protocols on using biomonitoring effectively in the event of suspected chemical exposure incidents.

A further section includes an update on the Children's Environment and Health Strategy, which is part of the WHO plan.

Dr Robert Maynard also presents two articles, one on 'concentration, exposure and dose', and the other looking at particles as air pollutants.

28th International Symposium on Halogenated Persistent Organic Pollutants

Dioxin 2008

August 17th-22nd 2008

At the International Convention Centre, Birmingham



For the first time in the history of this symposium (the premier meeting in the field of persistent organic pollutants), *Dioxin 2008* will be held in the United Kingdom. There will be a full scientific programme over the five days of the conference, covering all aspects of dioxins, “Stockholm” POPs, brominated flame retardants, perfluorinated chemicals, and “emerging” contaminants. The sources, levels, toxicology, and significance of POPs are of particular concern, and contributions in this area are especially welcome. All submitted papers will be reviewed, and, if accepted, will be included in the conference proceedings (*Organohalogen Compounds*).

The **RSC's OETG** will be supporting this event through sponsoring registration fees, travel and accommodation costs for students and early-stage researchers. Note that the deadline for submission of abstracts to this conference is likely to be early April 2008.

Anyone interested in receiving a bursary for attending this event should send their CV and their proposed abstract for either an oral or a poster presentation to:

Kate Jones, OETG Secretary (e-mail: kate.jones@hsl.gov.uk)

at the same time as submitting their abstract to the conference organisers.

For further details on the conference, to register, and to book hotel accommodation, visit www.dioxin2008.org

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Chemists poke holes in ozone theory

As the world marks 20 years since the introduction of the Montreal Protocol to protect the ozone layer, *Nature* has learned of experimental data that threaten to shatter established theories of ozone chemistry. If the data are right, scientists will have to rethink their understanding of how ozone holes are formed and how that relates to climate change.

The Montreal Protocol stopped the production and consumption of most ozone-destroying chemicals. But many will linger on in the atmosphere for decades to come. How and on what timescales they will break down depend on the

molecules' ultraviolet absorption spectrum, as the energy for the process comes from sunlight. Molecules break down and react at different speeds according to the wavelength available and the temperature, both of which are factored into the protocol.

So Markus Rex, an atmosphere scientist at the Alfred Wegener Institute of Polar and Marine Research in Potsdam, Germany, did a double-take when he saw new data for the break-down rate of a crucial molecule, dichlorine peroxide. The rate of photolysis of Cl_2O_2 reported by chemists at NASA's Jet Propulsion Laboratory

[1], was extremely low in the wavelengths available in the stratosphere — almost an order of magnitude lower than the currently accepted rate.

Rex says. “If the measurements are correct we can basically no longer say we understand how ozone holes come into being.” What effect the results have on projections of the speed or extent of ozone depletion remains unclear.

The rapid photolysis of Cl_2O_2 is a key reaction in the chemical model of ozone destruction developed 20 years ago [2]. If the rate is substantially lower than previously

thought, then it would not be possible to create enough aggressive chlorine radicals to explain the observed ozone losses at high latitudes, says Rex. The extent of the discrepancy became apparent only when he incorporated the new photolysis rate into a chemical model of ozone depletion. The result was a shock: at least 60% of ozone destruction at the poles seems

to be due to an unknown mechanism, Rex told a meeting of stratosphere researchers in Bremen, Germany, last week.

QUIRIN SCHIERMEIER

References

1. Pope, F. D. et al, *J. Phys. Chem. A*, 2007, **111**, 4322-4332.

2. Molina, L. T. & Molina, M. J., *J. Phys. Chem.*, 1987, **91**, 433-436.

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(See also Francis Pope's article, p. 10, above).

RSC | Advancing the
Chemical Sciences

New journal on the environment to be published by the Royal Society of Chemistry

Energy & Environmental Science

In summer 2008, the RSC will publish a new journal on the environment, *Energy & Environmental Science*. Introducing the new journal, Dr Robert Parker, Managing Director of RSC Publishing commented 'The challenges relating to energy and environmental science that face the world today are complex. Research in the chemical sciences – from alternative fuels to environmental impacts – and from climate change to energy conversion and storage – underpins all the work that is so important to the future of our world. RSC Publishing recognises the significance of this research by launching *Energy & Environmental Science*.'

Energy & Environmental Science will link all aspects of the chemical sciences by publishing research relating to energy conversion and storage, alternative fuel technologies, and environmental science. It will have monthly issues containing topical

reviews and original research as communications and full papers.

By recognising the complexity of issues and challenges relating to energy and environmental science, it is expected that *Energy & Environmental Science* will provide a forum for work of an interdisciplinary nature across both the (bio) chemical sciences and chemical engineering disciplines.

From its launch, the latest issue of *Energy & Environmental Science* will be made freely available to all readers via the website. During 2008 and 2009, free access to previous issues of the journal will be available following a simple registration process.

Professor Nathan Lewis has been appointed chair of the Editorial Board for *Energy & Environmental Science*.

'Energy is the most important scientific and technological challenge facing humanity in the twenty-first century. Energy security and environmental security have come to the forefront of both global and national priorities,' commented **Professor Lewis**. '*Energy & Environmental Science* aims to

bridge the various disciplines involved with energy and the environment, providing a forum for disclosing research results and discourse on this critical field.'

Prof. Lewis is the George L. Argyros Professor of Chemistry at the California Institute of Technology (Caltech). After receiving his PhD in Chemistry from MIT, he spent 6 years at Stanford. He moved to Caltech in 1988, becoming a Professor in 1991. He has served as the Principal Investigator of the Beckman Institute Molecular Materials Resource Center at Caltech since 1992.

Professor Lewis' research interests include light-induced electron transfer reactions, both at surfaces and in transition metal complexes, surface chemistry and photochemistry of semiconductor/liquid interfaces, novel uses of conducting organic polymers and polymer/conductor composites, and development of sensor arrays that use pattern recognition algorithms to identify odorants, mimicking the mammalian olfaction process.

Electronic Delivery of the *ECG Bulletin*

Would you like to download your copy of the *ECG Bulletin* electronically as a pdf instead of being sent the printed bulletin? Or, perhaps, your preference is to receive both the printed and pdf versions? More than 70% of our Members are now contactable by email

and, to reduce costs, the ECG is proposing to email a link to a Members' only area of the RSC where the Bulletin may be downloaded. Members who are not contactable via email or non-respondents would of course continue to receive the printed

version. Jo Barnes (ECG Honorary Secretary) will be emailing you to obtain your views but if you would like to register your opinion, please email her at jo.barnes@cornwall.ac.uk or write to the address on the front cover.

News of the Environment, Sustainability and Energy Forum (ESEF) in 2007

Sustainable water

Perhaps the most important event of a busy and successful year for the ESEF was the launch of the RSC report "Sustainable Water: Chemical Science Priorities". The report highlights the key role of the chemical sciences in driving future developments in water management, nationally and internationally. The report's scope encompasses the entire hydrological cycle with an emphasis on human activity, particularly on managing domestic, industrial and agricultural water use, contamination, and climate change. The report summarises the current situation and recommends future developments as well as the processes needed for these to be realised.

The report is intended to provide guidance to policy makers and funding bodies on the challenges and key priority areas for the chemical sciences, across the hydrological cycle, that will deliver the technologies, infrastructure, skills and stakeholder education for sustainable water management. The report focuses on presenting sound scientific evidence to support its key recommendations.

Web link: www.rsc.org/water

Fuelling the future

The RSC has also launched a report on sustainable transport entitled "Fuelling the Future". This publication is based on a series of workshops that were held at the RSC in April and May 2007. It reflects a number of expert views from academia, research and technology organisations, the motor industry, the chemicals industry and other key stakeholders. This is a summary of those views which, alongside the King

Review, aims to spark debate and contribute towards a realistic low carbon transport innovation strategy.

Reducing the CO₂ emissions from passenger cars is an important part of a wider strategy to reduce emissions from the power generation, industrial, transport and domestic energy sectors. The RSC has been actively campaigning since 2005 to demonstrate the vital role that the chemical sciences will play in the provision of safe, clean, affordable and secure energy. The RSC's position is laid out in the report "Chemical science priorities for sustainable energy solutions".

Web link: www.rsc.org/ftf

Sensors for the Atmosphere

ESEF has continued to make good progress on the Sensors for the Atmosphere project. The project aims to identify current and future challenges in this area and to bring together the relevant people and communities to propose solutions. A workshop was held at the Zoological Society in November 2007 that examined the challenges and technology transfer opportunities between researchers working on atmospheric sensors and those working in the defence and medical sectors. The steering group is currently considering further activities in 2008. If you have any suggestions please contact Yvonne Hübner (huebner@rsc.org)

Public consultations

The ESEF has responded to several public consultations in 2007. Perhaps the most important was the joint response between the RSC and several other learned and professional Societies and academic institutions to the Defra

'managing radioactive waste safely' consultation. The response calls for a significant public and media engagement programme to raise awareness of a radioactive waste repository. The response also states that public understanding of scientific uncertainty and risk is currently very poor and that this must be addressed. The RSC has since been involved in positive and constructive discussions with Defra concerning the joint recommendations and we hope to work with them in 2008.

Web link: <http://www.rsc.org/ScienceAndTechnology/Policy/Documents/EnergyEnvironment.asp>

Management of the ESEF

Finally, I would like to announce that I am leaving the RSC at the end of December in order to take up the position of National Energy Research Network manager at the UK Energy Research Centre* starting in January 2008. I would like to extend my thanks to the all the members of the Environmental Chemistry Group for making my job at the RSC hugely rewarding and great fun. I hope you all have a very productive 2008!

If you have any RSC or ESEF-related queries, please contact Yvonne Hübner (huebner@rsc.org) who will be looking after ESEF-related projects while the RSC seeks a new ESEF Manager.

*Web link: <http://www.ukerc.ac.uk/NERN/NationalEnergyResearchNetwork.aspx>

Dr JEFF HARDY
December 2007

Meeting report

The importance of indoor air

The RSC's Automation and Analytical Management Group held a meeting on "The importance of indoor air" at the Society of Chemical Industry, Belgrave

Square, London on December 13th and 14th 2007. Some 40 delegates attended.

Primary issues around the topic of indoor air were discussed. For instance,

on average in Europe most people spend 90% of their time indoors. This begs the question as to why the health risks of indoor air have not yet been as clearly associated with indoor air quality as the health risks which are

associated with outdoor air? (**Dimitrios Kotzias**, Joint Research Centre, Ispra, Italy, “Health risks from indoor air pollutants”).

However, evidence does exist that in 2000, 1.5 million deaths (2.7% of the global burden of disease) were associated with solid fuel use and this aspect of indoor air pollution is one of the ten most important threats to public health (**Michael Krzyanowski**, WHO, Bonn, Germany, “Health issues”). Chiefly these deaths occur in developing countries and are linked to carbon monoxide exposure; solutions lie in appropriate technological interventions in things such as ventilation and fuel quality.

In the first world, indoor air quality generally has a wider range of problems which are not so easily prioritised. However, it is worth noting that the chronic long-term effects of sub-acute exposure to carbon monoxide poisoning are observed more frequently in the UK than would be expected in a developed economy. Like many aspects of indoor air this is linked to weak enforcement of legislation by regular monitoring. (**Bob Maynard**, HPA, “A UK perspective”; **Martin Liddament**, VEETECH Ltd., Coventry, “Architectural and building services design to minimise indoor air pollution”).

Over and above the basic issues of poor ventilation and heating, VOCs did attract attention in the conference since the variety and profusion of these in indoor air is extensive – and the processes of modelling, monitoring, sampling, and quantitatively analysing for these species is an irresistible attraction for chemists. (**Nicola Carslaw**, York, “A new detailed model for indoor air chemistry”; **Jan Kristensson**, Chemik Lab, Sweden, “What are we monitoring?”; **Erik Uhde**, Braunschweig, Germany, “Emissions from materials and their impact on indoor air”; **Olivier Ramalho**, Centre Scientifique et Technique du Batiment, France, “Indoor air quality in French dwellings”).

What is difficult to see is the case for the prioritisation of VOC monitoring in the context of indoor air. There is “...no clear evidence that long-term exposure to commonly measured

indoor levels [of VOCs] represents a health risk, apart from a few examples referring to differences in human susceptibility” (**Dimitrios Kotzias**, *op.cit.*).

Although VOC concentrations may be higher indoors than outside (e.g. aldehyde levels inside public buildings and kindergartens were 7 to 8 times higher than outside; total VOCs inside public buildings vary from 8 to 281 $\mu\text{g m}^{-3}$ whereas outdoor concentrations vary from 7 to 153 $\mu\text{g m}^{-3}$), there is little evidence for their direct impact on public health at the concentration levels found indoors (**Dimitrios Kotzias**, *op.cit.*).

The odours associated with VOCs odours may be problematic in terms of discomfort and nuisance (**Peter Wolkoff**, National Research Centre for the Working Environment, Denmark, “What species should we be monitoring?”; **Erik Uhde**, *op.cit.*), but it is conceptually easy to see that these problems and many others associated with indoor air could be solved by the UK government and the EU promulgating more directive statutory building prescriptions which specify ventilation criteria.

The problems with tobacco smoke dominate by at least two orders of magnitude the problems associated with other forms of indoor air pollution. The dramatic reduction in tobacco-related air pollution after the UK government’s legislation is an exemplar of how effective such public health interventions can be; albeit somewhat overdue. (**Ivan Gee**, John Moores, Liverpool, “Environmental tobacco smoke: monitoring strategies and Measurement”). However, the situation in private homes (and its impact on non-smokers in at-risk groups such as the very young and elderly) remains.

The particular problems associated with the potential for ingress into homes of particulates containing heavy metals from load bearing soil (i.e. of geological origin) or from contaminated land were discussed in relation to arsenic. The difficulties in estimating the impact on individual health, the costs of performing statistically robust sampling, and the potentially huge variations in local exposure provide some interesting considerations for future monitoring of such elements in

airborne dispersion. (**Jo Barnes**, Cornwall College, “Mispickel and Wasserkies – the health risks of resuspended arsenic in Cornwall”).

Persistent organic pollutants (POPs) as a subset of VOCs include PCBs (polychlorinated biphenyls), BFRs (brominated flame retardants, such as polybrominated diphenyl ethers (PBDEs)), and hexabromocyclododecanes (HBCDs). PCBs provide an interesting case study, partly because in spite of the manufacture of PCBs in the UK having ceased some 30 years ago, indoor air concentrations have not declined significantly since the 1990s and partly because the outdoor air concentrations of PCBs seem to be extensively driven by degassing from indoor environments. This has implications for the continuance of indoor exposure for the future. (**Stuart Harrad**, Birmingham, “Indoor contamination with Persistent Organic Pollutants – implications for human exposure”).

Indoor air pollution needs more research, and consequent on this, more attention by central government. The research does however need to have a clear agenda, one which is focused on identifying both immediate, effective interventions and utilitarian solutions, and one which is prioritised in relation to maximising the impact of the funding available on public health. This conference evidenced the need for such an agenda to be established.

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The RSC Library will close for refurbishment at the end of May 2008 and will reopen as a Chemistry Centre. More detailed information on the forthcoming changes will appear in issues of *Chemistry World* and *RSC News*.

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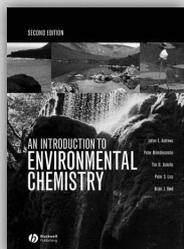
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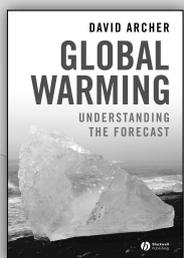
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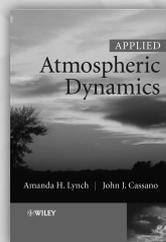


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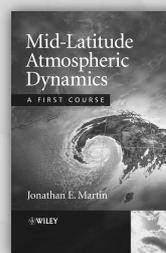
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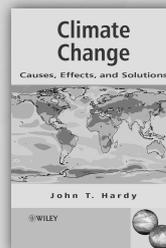
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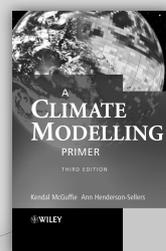


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