

THE ROYAL SOCIETY OF CHEMISTRY ENVIRONMENTAL CHEMISTRY GROUP

Bulletin

RSC Advancing the Chemical Sciences

July 2006

RSC Advancing the Chemical Sciences

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The University of Leeds FAGE instrument located at the British Antarctic Survey Halley Station in 2005. Measurement of atmospheric hydroxyl radicals using FAGE, p. 3. (Photograph courtesy of Dr William Bloss, University of Leeds).

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News of the Environmental Chemistry Group

The Group's activities in 2005 and 2006 have been focused in three main areas: the *ECG Bulletin*, the Group's web page and our Distinguished Guest Lecture. In addition, we collaborated in the highly successful joint SCI and RSC meeting in March 2005 on *Pharmaceuticals in the Environment*.

ECG Bulletin

Rupert Purchase continues to edit the Bulletin and is assisted in gathering content by Ruben Sakrabani. They have continued to produce an excellent product and would welcome suggestions from the members of the Group for topics and potential authors for future contributions. Back copies of the bulletin are available at http://www.rsc.org/Membership/Netwo rking/InterestGroups/Environmental/bu lletin.asp.

ECG Web page

The ECG Web page has been reorganised and maintained by Chris Harrington. Again, we would welcome comments and suggestions about Web content related to the Group's environmental chemistry remit from members.

Distinguished Guest Lecture

The 2005 and 2006 Distinguished Guest Lectures and accompanying symposia were coordinated by Mike Leggett and were both very well attended. The general title for the 2005 DGL was Metals in the environment: estimation. health impacts and toxicology, and the title for this year's meeting was The impact of climate change on air quality. At the 2006 DGL, Professor Michael Pilling, University of Leeds, became the first recipient of the ECG Distinguished Guest Lecturer Medal. The background to this new award is described on p. 20 of the January 2006 issue of the ECG Bulletin.

ESEF

The ECG continues to play an active role in the Environment, Sustainability and Energy Forum (ESEF). The ECG is represented on the Forum by Andrea Jackson and Brendan Keely. Jeff Hardy, the ESEF Manager, also attends ECG committee meetings, thereby helping to ensure a close working relationship between the ECG and the ESEF.

Future developments

Discussions with the ESEF and with Professor Michael Pilling, Chairman of

the RSC's Faraday Division, identified a gap in the way the RSC provides for the atmospheric chemistry community. The ECG has responded to this need by creating a specific position on the ECG committee for an atmospheric chemist. This initiative will lead to an increase ECG's involvement in the in atmospheric chemistry, and we hope that more atmospheric chemists will ioin the ECG and become active members of the Group.

For the 2007 DGL and Symposium, we are planning an all day event in March 2007 with the theme *Environmental chemistry in the polar regions*. Full details of this meeting will appear on our web page.

Acknowledgement

I would like to thank all of the members of the ECG committee for their good work during 2005 and 2006: Jo Barnes (Honorary Secretary), Andrea Jackson (Vice-Chairman and Honorary Treasurer), Leo Salter, Rupert Purchase, Chris Harrington, Mike Leggett, Ruben Sakrabani and Kim Cooke.

BRENDAN KEELY

Chairman, Environmental Chemistry Group, June 2006

Atmospheric chemistry research in the UK

'Global temperatures reach new high'

'US greenhouse emissions continue upward trend'

These headlines for two recent reports of environmental data from the USA provide further ammunition for those concerned about the climate and the checks and balances that control climate change. Understanding atmospheric chemistry is central to predictions of climate change, and this issue of the ECG Bulletin focuses on several aspects of recent research on the atmosphere. In the first of two articles by UK researchers, Shona Smith from the University of Leeds describes the measurement of hydroxyl radical concentrations in the atmosphere and the role of this oxidant in tropospheric chemistry.

Soils are important sources and sinks for the three main greenhouse gases, nitrous oxide, methane and carbon dioxide. In a second article, Ute Skiba and Peter Levy from the Centre of Ecology and Hydrology, Edinburgh review the microbial processes which generate these three gases and the environmental conditions which favour their emissions from, or uptake by, soil. The impact of climate change on air quality was the title for this year's Chemistry Environmental Group Symposium, which incorporated the ECG's 2006 Distinguished Guest Summaries of the Lecture presentations by the three speakers at the meeting, who all work in UK

Web sites that give useful guidance and data on air quality for legislators and environmental scientists alike are the subject of a review by **Alex Ledbrooke** from Cornwall College.

Changes to the polar ice caps have offered some of the most powerful televisual images of the consequences of climate change. The ECG's **2007 Distinguished Guest Lecture** and accompanying symposium to be held in March 2007 at Burlington House will explore the science behind those images under the general title *Environmental chemistry in the polar regions.*

The effect of climate change on coastlines provided the topics for a CoastNET meeting in The Hague earlier in 2006, which **Leo Salter** attended and now reports on for this issue of the *ECG Bulletin*.

universities, appear in this issue.

Global temperatures reach new high

Last year, 2005, was the warmest for over 100 years, according to the American space agency NASA. The global climate has now warmed by 0.6 degrees Celsius in the past three decades, it reported.

The five warmest years in the last century have occurred in the past eight years: 2005, followed by 1998, then 2002, 2003 and 2004. Warming is happening fastest in high latitudes of the northern hemisphere. This "rapid warming gives urgency to discussions about how to slow greenhouse gas emissions", the Agency stated.

But scientists at Manchester Metropolitan University are predicting that the rise in sea levels from global warming could be much lower than previously feared. Researchers say melting glaciers and ice caps will cause just a 0.1 m rise in global sea levels by 2100 - less than half the increase of several earlier predictions. However, they show that melting of glacial and mountain areas is accelerating fast, leading to flooding and land slides in mountainous regions such as Nepal.

The proceedings of a major international scientific conference on climate change held last year have been published in book form. The conference was organised by the UK government during its presidency of the G8 group of industrialised nations.

NASA:

www.nasa.gov/vision/earth/environmen t/2005_warmest.html; Manchester Metropolitan University: www.mmu.ac.uk/news/;

UK G8 Climate Conference: www.defra.gov.uk/news/2006/060130c. htm

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US greenhouse emissions continue upward trend

US emissions of greenhouse gases increased by 1.7% in 2004, the latest figures from EPA show. This increase

was due primarily to an increase in carbon dioxide emissions associated with fuel and electricity consumption. The figures are contained in the annual inventory required under the UN convention on climate change.

Total emissions of the six main greenhouse gases in 2004 were equivalent to 7075 million metric tonnes of carbon dioxide. These gases include carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, and sulfur hexafluoride. Fossil fuel combustion was the largest source of emissions, accounting for 80% of the total.

Overall, emissions have grown by 15.8% from 1990 to 2004, although the US economy has grown by 51% over the same period.

EPA: Inventory of US Greenhouse Gas Emissions and Sinks: 1990–2004, www.epa.gov/globalwarming/publicati ons/emissions

This news item is repoduced with permission from *J. Environ. Monit.*, 2006, **8**, 427.

Hydroxyl radical chemistry and the atmosphere

The most important oxidant in the atmosphere is the hydroxyl radical, OH. Reaction with OH begins the degradation of trace gases in the atmosphere, controlling hence their lifetime and potential to contribute to problems such as climate change and ozone depletion. The OH-initiated oxidation CO of and hydrocarbons in the presence of oxides of nitrogen also generates ozone, a constituent photochemical of smog. Improved understanding of the abundance and distribution of OH is therefore a key goal atmospheric chemistry of research. Shona Smith from of University Leeds the

explains more on hydroxyl radical chemistry and recent research on its role in atmospheric chemistry.

The OH radical is highly reactive and therefore its concentrations are low (~ 0.04 - 0.2 pptv (parts per trillion by volume) in the sunlit troposphere) and its chemical lifetime short (< 1 s). Therefore OH concentrations are determined by chemistry, not transport, and OH radicals are assumed to be under steady state conditions. These conditions allow comparisons between in situ measurements of OH and HO₂ (a closely coupled 'cousin' of OH, OH + $HO_2 = HO_x$) radicals with simple steady state calculations and more complex zero-dimensional box model constrained simulations. bv observations of longer-lived species such as NO_x (NO + NO₂), ozone and VOCs (volatile organic compounds). modelled Comparing OH with measurements provides a test of our understanding of the processes involved in the OH chain reaction (see **Fig. 1**). Findings can then be used to validate the chemical mechanisms which are applied to climate change and global chemistry models.

The most important OH production route in the sunlit troposphere is the photolysis of O₃ by wavelengths of light \leq 340 nm to produce electronically excited oxygen atoms, roughly 10% of which react with H₂O to produce OH. The major sinks for OH under clean conditions are CO, CH₄ and to a lesser extent VOCs, resulting in production of hydroperoxy radicals, HO_2 , and other peroxy radicals, RO_2 (R = alkyl group). HO_2 is also produced through reaction of OH with O₃ and photolysis of HCHO, and is recycled to OH through reaction with O₃ and NO. HO_x chain termination occurs via radical recombination reactions (HO₂ + HO_2 , $HO_2 + RO_2$ and $OH + HO_2$) and by reaction of OH with NO₂, the latter dominating in polluted air.

Figure 1 shows a simplified HO_x cycle.

July 2006

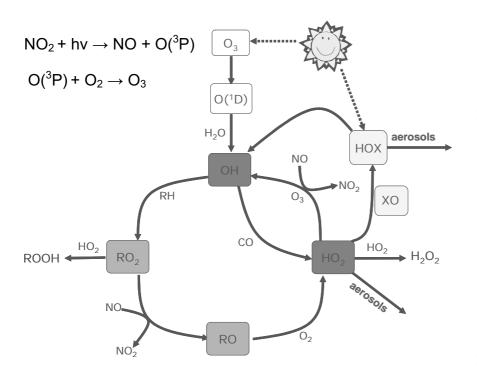


Figure 1: The catalytic cycle of OH in the troposphere involving not only the removal of trace gases but also the production and destruction of O_3 depending on NO_x concentrations. XO is a halogen oxide, where X = Br or I. R represents an alkyl group

OH is difficult to measure for several it is present reasons: in low concentrations, has a short atmospheric lifetime, localised concentrations and reacts quickly with surfaces. Therefore any technique employed to measure OH must be very sensitive, highly selective, fast and in situ. The most commonly employed technique for measuring OH is a low pressure onresonance laser induced fluorescence (LIF) technique known as FAGE (Fluorescence Assay by Gas Expansion) [1-4]. The technique employs 308 nm radiation, produced using variety of laser technologies, to excite OH radicals, which fluoresce; this emission (at 308 nm) is detected and used to quantify OH. It is also possible to simultaneously detect HO₂, by chemical conversion to OH through reaction with NO and subsequent detection by LIF. The FAGE technique is not absolute, requiring calibration using (VUV) vacuum-ultraviolet photolysis of H₂O by a mercury lamp coupled with O₃ actinometry.

To date the University of Leeds FAGE instrument has been successfully deployed on eleven field campaigns at various locations across the globe. During these campaigns measurements are made of a range of atmospheric species and parameters, along with meteorological data, which are used to constrain models. Such field work and later analyses of the OH and HO₂ data have led to many advances in our understanding of tropospheric chemistry. This report aims to give an overview of some of the recent discoveries made as a result of fieldwork, which have improved our understanding of the mechanisms that control OH and HO₂ in the atmosphere.

Halogen chemistry

Models tend to over-predict HO_2 due to missing HO_2 sinks. Recent studies have highlighted the significance of halogen chemistry to the HO_x cycle in marine air. Comparisons of modelled and measured HO_2 data in marine and Antarctic boundary layer air have demonstrated that halogen oxides, XO (where X = I, Br), significantly impact HO_x abundance through the reaction channels shown as part of the HO_x cycle in **Fig. 1**.

Some of the first co-ordinated tropospheric measurements of halogen monoxides with OH and HO₂ were made during the North Atlantic Marine Boundary Layer Experiment (NAMBLEX), which took place in the summer of 2002 at the Mace Head

Atmospheric Research Station, Ireland [5]. Sommariva et al (2006a) modelled HO_2 (and OH) using a zeromodel based on the dimensional comprehensive Master Chemical Mechanism (MCM), which overpredicted HO₂ by an factor of 3.0±0.9 compared to measurements (see Fig. 2). The influence of the reaction of HO_2 ΙΟ investigated with was by constraining the model to IO measured using long-path Differential Optical Absorption Spectroscopy (DOAS) [7]. Measured IO reached a maximum concentration of 4 pptv, resulting in reductions of up to 30% in modelled HO₂ compared to the base model (see Fig. 2). However, the model continued to significantly over-predict HO₂. This analysis used IO measured as the average across the DOAS beam path (8.4 km). Saiz-Lopez et al (2006), provide compelling evidence that IO concentrations at the HO₂ measurement site are an order of magnitude greater than the DOAS measurements due to local, coastal seaweed emissions of alkyl iodides and molecular iodine. Including IO×10 in the model reduced modelled HO_2 by up to 50%, resulting in relatively good agreement with measured HO₂ on most days (see Fig. **2**). The reaction of BrO with HO_2 had a qualitatively similar affect as IO further reducing HO₂ by up to 25%. Loss of HO₂ to BrO had a smaller direct affect upon HO₂ despite being measured with concentrations up to 7 ppt, because the rate coefficient for reaction of HO₂ with BrO is four times slower than that of IO.

The impact of these results is clear; if local IO really is a factor of 10 greater than the DOAS beam path average measurements, then combined with BrO, halogen chemistry would dominate the HO_x budget. Further evidence to support this theory was found when measurements of HO_x, IO and BrO were made in Antarctica during the CHABLIS (Chemistry of the Antarctic Boundary Layer and the Interface with Snow) summer intensive of 2005. Modelling of these data have shown that halogen chemistry dominated the HO_x budget with reaction of HO₂ with IO acting as the not only the main HO₂ sink, but also the main OH source, through the photolysis of the resultant HOI.

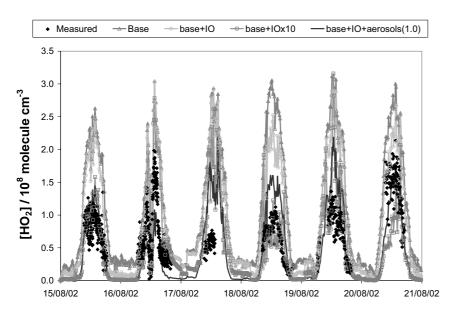


Figure 2: Diurnal profiles of measured HO₂ (black diamonds) and HO₂ modelled using several variants of a zero dimensional box model based on the Master Chemical Mechanism (MCM) from the NAMBLEX 2002 campaign in Mace Head, Ireland. Model calculations are shown from the base model (medium gray line, open triangles), base model including loss of HO₂ to IO (light grey line, open circles), base model including loss of HO₂ to IO×10 (medium grey line, open squares) and base model including both loss of HO₂ to IO and aerosols (dark grey line) [7].

Heterogeneous losses

Other recent studies into model overprediction of HO₂ [6, 9, 10] have illustrated that heterogeneous uptake of HO₂ onto aerosols can significantly reduce modelled HO₂. More accurate constraints of heterogeneous losses in models are now possible due to detailed field measurements of size-dependent chemical and physical properties of aerosols [11]. These data, along with laboratory measurements of the HO₂ uptake coefficient, γ_{HO_2} , are used to pseudo-first-order calculate rate coefficients for the uptake of HO₂ onto particles, k_{aerosol}. The aerosol of these calculations is accuracy currently limited by the large uncertainty in $\,\gamma_{_{HO_2}}$. Modelling of ${\rm HO_2}$ data from NAMBLEX was used to investigate the maximum effect of including heterogeneous losses of HO₂ in the model using the maximum theoretical value for γ_{HO_2} of 1.0. These results showed that when γ_{HO_2}

= 1.0 modelled HO_2 was reduced by up to 50% compared to the base model. Data were modelled for six days with good agreement between model and measurements observed on two days, an under-prediction in HO_2 on one day whilst the model continued to overpredict HO_2 on the remaining three days.

Modelling of data from the NAMBLEX campaign illustrates that the reaction of HO₂ with IO or the uptake of HO₂ onto aerosols (γ_{HO_2} = 1.0) cannot in isolation account for the overprediction of HO₂ by the model. When both HO₂ loss routes were included in the model simultaneously (see Fig. 2), there was seen to be good agreement between the model and measurements. Further to this Sommariva et al (2006a) find that if the hypothesis that the IO concentrations at the HO₂ measurements site are a factor of 10 greater than those measured as the average across the DOAS beam path [8], then γ_{HO_2} must be significantly smaller than 1.0 (consistent with the laboratory findings of Thornton and Abbatt, 2005 [12]) as otherwise HO₂ would be significantly under-predicted by the model.

OH reactivity – revealing unknown OH sources and sinks

Models have over-predicted [OH], especially in polluted air, mostly due to the underestimation of OH sinks. As it is not possible to measure every OH sink, instrumentation has been developed to directly measure the total OH reactivity or loss rate, k', which is the sum of all OH sinks (Eq. 1) or the inverse OH lifetime, τ (Eq. 2).

$$k' = \sum k_{OH+X} [X]$$
 (Eq. 1)
$$\tau = \frac{1}{\sum_{i} k_{OH+Xi} [X]_{i}} = \frac{1}{k'}$$
 (Eq. 2)

where k_{OH+X} is the second order rate constant for the reaction of OH with sink X.

The University of Leeds OH reactivity instrument is a large atmospheric pressure flow tube which contains a translatable injector housing an OH source (VUV-photolysis of H₂O). A sample flow of ambient air is drawn into the flow tube and ambient OH is lost on the sample line. High concentrations of OH radicals are then produced by the injector, mixed turbulently into the air flow and sampled downstream using a FAGE cell. Drawing the OH injector away from the detection cell gives an exponential decay of OH radicals as they react with constituents of the ambient air. The OH reactivity (s⁻¹) is then found as the negative slope of the logarithm of the OH signal as a function of time.

OH reactivity measurements can be used to test our understanding of OH sources and sinks. Modelling OH reactivity and comparing to measurements quantifies the degree to which the model is missing OH sinks. During the summer 2004 Tropospheric Organic Chemistry (TORCH) experiment, at the Weybourne Atmospheric Observatory in Norfolk, a model based on the MCM and constrained to measured species, underpredicted OH reactivity by an average of 40%. The contributions of the main OH sinks to the average measured OH reactivity (9.3 s^{-1}) were calculated using the average measured concentrations of sinks and their rate constants for

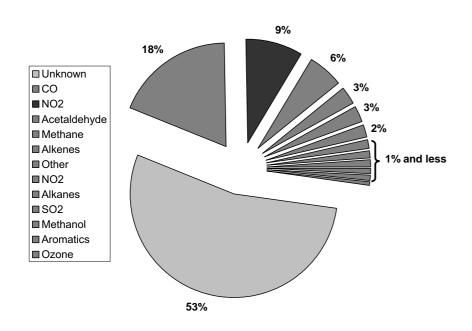


Figure 3: Data from TORCH 2004 showing contributions of the major OH sinks to the average measured OH reactivity (9.3 s^{-1}), calculated using the average measured concentration and their rate constants for reaction with OH.

reaction with OH (see Fig. 3). This large unexplained revealed а component to OH loss of ~54%. Contributions to this unknown proportion of OH loss are likely to come from unmeasured VOC species. Large unexplained components to OH loss have also been observed by Di Carlo et al (2004) in a northern Michigan forest and Sadanaga et al (2004) in suburban Tokyo. In these studies the unknown portions of OH loss were attributed to unmeasured biogenic and anthropogenic VOC species respectively.

OH reactivity measurements can also be used to investigate missing OH sources. OH is in the steady state and hence its rate of production is equal to its rate of loss. Calculations of steady state OH concentrations can be made by dividing calculated OH production rates by measured OH reactivities, k'(Eq. 3). Measured OH data from the TORCH 2004 campaign, were compared to steady state OH calculated using measured OH reactivities and OH production rates from O₃ photolysis and recycling of HO₂ through reaction with O_3 and NO (see Eq. 4, where $i(O^1D)$ is the rate of photolysis of O₃ by sunlight to produce $O(^{1}D)$ and f is the fraction of $O(^{1}D)$ that reacts with $H_{2}O$ to produce OH). Steady state calculations were able to simulate the shape and the levels of the OH diurnal profile relatively accurately on some days, although on the majority of days the calculations significantly under-predict OH. This may be because missing OH sources are significant during these periods. Recent studies suggest that contributions to the missing OH sources are likely to be O₃-alkene reactions and HONO photolysis. Measurements of OH and HO₂ made at the same site in Birmingham during the summer and winter Pollution of the

$$[OH]_{ss} = \frac{P(OH)}{k'}$$
(Eq. 3)
$$P(OH) = 2f O_3 j(O^1D) + (k_{HO_2+O_3}[O_3] + k_{HO_2+NO}[NO])[HO_2]$$
(Eq. 4)

Urban Midlands (PUMA) campaigns [15] found O₃-alkene reactions sustained the winter radical pool. This meant that despite a factor of 15 reduction in OH production from O₃ photolysis in winter, OH concentration were only a factor of 2 less than during summer. Further evidence to support photolytic sources of OH that are significant to OH production when ultra-violet light intensity is low, was found where measured OH has a wider diurnal profile than that of steady state OH calculated using O₃ photolysis as the main OH source. This is likely to be due to production of OH through photolysis of HONO which is photolysed at longer wavelengths of light than O₃. Several recent studies [16-17] have illustrated the importance of HONO as an OH source. A recent publication by Stemmler et al (2006) [18] indicates that photolysis of HONO could contribute up to 50% of OH production in the lower 100 m of the atmosphere.

Conclusions

Recent field campaigns have produced comprehensive data sets, which through comparison with models, have allowed significant improvements in understanding of HO_x chemistry. Simultaneous measurements of HO_x and the halogen oxides, IO and BrO, in marine and Antarctic boundary layer air have shown the impact these species can have on HO_x abundance, by providing not only an additional sink for HO₂ but also a source of OH through HOX photolysis. These studies have also highlighted the need for better spatial resolution in the halogen oxide measurements than can be provided by long path DOAS. This summer as part of the NERC (Natural Environment Research Council) funded Reactive Halogens in the Marine Boundary Layer (RHaMBLe) program, the University of Leeds FAGE and DOAS instruments will make simultaneous IO measurements, in an attempt to improve understanding of the spatial resolution of this radical.

Using a better treatment of heterogeneous losses within models has shown that uptake of HO_2 onto aerosols plays an important role in free-radical chemistry. However, further studies of the physical and chemical properties of aerosols, and in particular, the rate coefficients for the heterogeneous

uptake of HO_2 radicals onto realistic 5. aerosol surfaces, are required to further our understanding.

Measurements of the total OH reactivity are key to assessing our understanding of OH source and sinks. Data from the TORCH 2004 campaign revealed а significant unknown proportion of the OH sinks, which are likely to arise from unmeasured VOC species. Comparing steady state OH concentrations, calculated using measured OH reactivities and an OH production rate from O₃ photolysis and recycling of HO₂ through reaction with O_3 and NO, revealed that other OH sources, such as the reaction of O_3 with alkenes and HONO photolysis, are potentially important.

Acknowledgements

Thanks to all of those involved in both the measurement and modelling of HO_x radicals included in this article. Particular thanks to all members of the Leeds FAGE team (past and present). Funding was provided by the Natural Environment Research Council.

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June 2006

Shona Smith's research into HO_x measurements and chemistry is being carried out under the supervision of Professor Dwayne Heard and forms part of the work of the **Chemical Dynamics Group** within the School of Chemistry at Leeds University. More information on this Group and the FAGE instrument is available from http://www.chem.leeds.ac.uk/. A complementary article on the measurement of tropospheric hydrogen peroxide and hydroperoxides was published in the July 2004 issue of the *ECG Bulletin*.

Greenhouse gas emissions from soil ecosystems

Our soils are important sources and sinks for the three main greenhouse gases nitrous oxide (N_2O) , methane (CH_4) and carbon dioxide (CO₂). Α pristine. undisturbed soil is almost carbon neutral, although natural wetland ecosystems are a significant source of methane and tropical forests a significant nitrous source of oxide. Anthropogenic disturbance of natural ecosystems has led to increases in greenhouse gas emissions, which have escalated intensification since the of agriculture and land management - contributing significantly to the global rise in greenhouse gas concentrations. Ute Skiba and Peter Levy from the Centre for Ecology and Hydrology, Edinburgh, describe the interplay between soil and the atmosphere and each of the three greenhouse gases, N₂O, CH₄ and CO₂.

Introduction

Since the industrial revolution carbon dioxide concentrations have increased from about 280 ppm in 1750 to 367 ppm in 1999, methane from around 770 ppb to 1891 ppb and nitrous oxide from 270 ppb to 410 ppb. Concentrations of all three greenhouse gases are still rising (Table 1). The energy sector, i.e. fuel combustion, is mainly responsible for this rise, and now contributes to over 80% of all UK greenhouse gas emissions. The second largest source of greenhouse gases (7% annual UK emissions) is agriculture, principally nitrous oxide emissions from fertilised soils and methane emissions from enteric fermentation in ruminants. The sources methane soil of are predominantly natural and agricultural wetlands (mainly rice paddies). In the UK wetlands are predominately natural ecosystems, such as blanket bogs. Large areas of these are only found in Scotland and North Wales. Established, undisturbed soils are a sink for carbon dioxide. This sink, however, is turned into a source when the soil is disturbed by cultivation, drainage or clear felling.

All three greenhouse gases are produced in soil by microbial processes. These processes appear to be the same in pristine natural soils as in intensively managed agricultural soils and are also the same in all climate zones of our planet. The soil and environmental conditions which will favour nitrous oxide, methane or carbon dioxide emissions or uptake are outlined in greater detail below.

Nitrous oxide

Soil is the single largest source of nitrous oxide globally (Climate Change, 1994). For example, in the UK, soils are responsible for more than 70% of the total annual nitrous oxide emission. Other important sources of nitrous oxide are adipic acid and nitric acid production and fuel combustion (Baggott *et al*, 2006). Vehicle emissions of nitrous oxide have risen sharply since the installation of catalytic converters, whereas industries have managed to significantly reduce their nitrous oxide emissions.

Nitrous oxide is produced in soil by two microbial processes: nitrification and denitrification (Bremner, 1997). Nitrification is the aerobic oxidation of ammonium to nitrate and is carried out by a very specific group of microorganisms that use carbon dioxide as sole carbon source. When oxygen levels in the immediate vicinity of the microorganims are insufficient for complete oxidation to nitrate, the organisms will produce nitrous oxide instead.

Denitrification, the anaerobic reduction of nitrate to nitrous oxide and dinitrogen, on the other hand, is carried out by a wide range of soil microorganisms. Many of these can function in aerobic and anaerobic environments and relying on organic carbon compounds for their carbon source. Under anaerobic conditions nitrate is reduced to nitrous oxide or dinitrogen in order to generate electrons required for energy the production inside the microbial cell.

The key variables controlling the rate of microbial production and emission of nitrous oxide are substrate availability (mineral nitrogen), temperature, soil water content, and for denitrification also labile organic compounds (Skiba and Smith, 2000). Under optimal conditions nitrous oxide emissions are directly related to the soil mineral nitrogen concentrations. Therefore, any process that increases the mineral N concentration in soil has the potential to increase nitrous oxide emissions. Agricultural soils fertilized with nitrogen, mineral or organic forms are important sources and emit most of our nitrous oxide. The response to fertiliser application under optimal conditions can be rapid, within hours. Increased nitrous oxide emissions can he expected for 2 to 3 weeks, before returning to background slowly conditions of emissions $< 1 \text{ kg } N_2\text{O-N}$ $ha^{-1}y^{-1}$ (**Figure 1**).

Soil mineral nitrogen concentration can also be increased by ploughing, burning, clear felling a wooded area, pulsing (the first rainfall or irrigation onto dry soil), freeze - thaw cycles and atmospheric nitrogen deposition. All these activities can produce a pulse of high nitrous oxide emissions, which can contribute considerably to the total annual emission. For example, the pulsing effect can be an important source of nitrous oxide in countries that experience very cold winters (i.e. northern countries in continental Europe), or have distinct wet and dry seasons (i.e. Mediterranean and African

Table 1: The UK greenhouse gas budget for 2004(http://www.naei.org.uk/reports)

Source	Carbon dioxide	Nitrous oxide	Methane
	kt CO ₂	kt N ₂ O	kt CH ₄
Energy	547073.65	28.69	583.26
Industrial Processes	11367.99	13.01	2.84
Agriculture		85.60	889.60
Land use change and forestry	-1941.56	0.01	0.80
Waste	451.74	4.04	703.81
Other	3310.77	0.25	11.01
Total	560262.60	131.59	2191.31

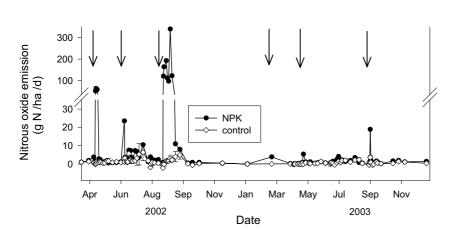


Figure 1: Nitrous oxide emissions from cut grassland plots in SE Scotland, fertilised with NH_4NO_3 at a rate of 100 kg N ha⁻¹ on three occasions, April, June, and August 2002 and 2003. Nitrous oxide emissions increased within one day of fertiliser application (•) and elevated emissions were measured for 7-20 days after fertiliser application in relation to emissions from control plots not receiving N fertiliser (◊) (Jones et al, 2005).

countries). Large pulses of nitrous oxide are released when frozen soils defrost or immediately after the first rains onto very dry soil. The mechanism is the same in both situations. Drying and freezing kill a large percentage of the microbial community releasing a readily available supply of nutrients for the surviving microbial population to utilise when conditions (temperature or water availability) improve.

Atmospheric deposition of nitrogen species can provide a significant source of nitrogen to the soil environment, especially to soils that are not fertilised. In Europe nitrogen deposition rates range from $< 2 \text{ kg N ha}^{-1} \text{ y}^{-1}$ in pristine environments to $> 80 \text{ kg N} \text{ ha}^{-1} \text{ y}^{-1}$ immediately adjacent to large point sources of pollution, such as industrialised conurbations (NO_x) or intensive livestock management (ammonia) (Fowler et al, 1999). Rates of nitrogen deposition are also elevated at high altitudes due to a higher incidence of hill cloud. This effect is exacerbated by the presence of forests, which are very efficient in capturing cloud water. For agricultural, nitrogen fertilised, soils the additional, usually much smaller, input of nitrogen by deposition is not an issue. However, for soils not receiving nitrogen fertilisers, such deposition rates can provide a significant source of mineral nitrogen and have been shown to enhance emissions of nitrous oxide. For example, in a spruce forest in Germany, where nitrogen deposition rates were 40 kg N ha⁻¹ y⁻¹, mean monthly nitrous oxide emissions ranged from 4 to 16 μ g N m⁻² h⁻¹, but in a comparable spruce forest in 'cleaner' Ireland with deposition rates < 10 kg N ha⁻¹ y⁻¹, nitrous oxide emissions only ranged from -0.5 μ g (net uptake) to 2 μ g (net emission) N m⁻² h⁻¹ (Butterbach-Bahl *et al*, 1998).

Many experiments in the laboratory and field have shown a direct linear relationship between nitrogen additions and nitrous oxide emissions. This direct relationship has been adopted by the Intergovernmental Panel of Climate Change (IPCC) to provide a simple methodology for countries to calculate their annual nitrous oxide emissions. For example, it is assumed that 1.25%

of the mineral nitrogen fertiliser applied to agricultural soils and 1% of the atmospheric nitrogen deposition is emitted as nitrous oxide (Houghton et al, 2001). This approach provides an excellent broad picture of the contribution of soils to the countries total emission rate. The uncertainties in this estimate, however, are very large, partly because other important variables environmental rainfall. temperature and land management are not taken into account.

The importance of variables other than nitrogen in determining the magnitude of the emission is shown in **Figure 2**. Identical rates of nitrogen fertiliser additions to cut grassland in South East Scotland stimulated different nitrous oxide peaks in response to the six fertilisation events in 2002 and 2003. Differences in rainfall patterns, in particular at times of fertilisation, differences in soil temperature and differences in nitrogen demand at various growth stages of the crop all contributed to the variability in nitrous oxide emissions.

Models have been developed to take into account the complex relationship between rates of nitrous oxide emission and environmental variables. One widely used promising model, originally written for the main anthropogenic source of nitrous oxide, agricultural soil. is DNDC (Denitrification Decomposition) (Li. 2000). As all complex models, a lot of on information the crop, soil. meteorology management, etc. is required. Unfortunately these data are not available for all our soils and at present cannot replace the simple

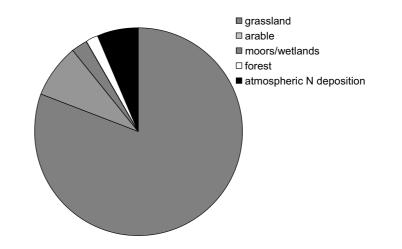


Figure 2: The percentage contribution of the dominant soil ecosystems to the total annual emission of nitrous oxide from soils in Great Britain.

approach adopted by the IPCC. At CEH, we have developed a simple multi-linear regression model, which takes into account the three main variables, nitrogen input, rainfall and soil temperature. We have used this model to calculate nitrous oxide emissions from the different land uses in Great Britain (Sozanska *et al*, 2002).

In the UK, grasslands are the largest soil source of nitrous oxide and together with manure from housed and grazed animals returned to grassland we have estimated annual emissions at 74 kt nitrous oxide (>80% of total soil emissions). Per unit area grassland emissions are larger than from fertilised arable land, because a) grasslands receive larger rates of mineral fertiliser and manure, b) grasslands occur in high rainfall regions, c) grazed grasslands have compacted soils. Such conditions are all favourable for nitrous oxide production. The location of intensively managed grasslands is mainly in the western wetter part of Great Britain, for which we have estimated larger annual rates of nitrous oxide emissions than the eastern part of the country (Sozanska *et al*, 2002). The contribution of arable land to the total nitrous oxide emission (8%) is of importance as nitrogen similar deposition derived nitrous oxide emission rate (6%). In Scotland, the fertile soils in Fife and East Lothian, capable of producing a wide variety of arable crops contribute significantly to the local nitrous oxide emission. Forests, heath and moorlands contribute less than 5% to the total soil emission.

Methane

At the global scale the largest methane sources are natural wetlands (21% of the global annual total emission), of fermentation farmed enteric livestock (15%) and rice paddies (11%). Methane is produced by strictly anaerobic microorganims (methanogens). Production is therefore restricted micro-habitats where to oxygen diffusion is inhibited, for example by high water content in rice paddies or inside the rumen of ruminant livestock. The primary factors controlling the rate of methane production in wetlands and rice paddies are water table height and temperature. Plants play a significant role in the transport of methane from the zones of production to the atmosphere. For example, surface water

on a blanket bog in Caithness emitted 10 times more methane when vegetated with *Menyanthes trifoliata* (Bog-bean) compared to adjacent non vegetated parts of the same surface water (MacDonald *et al*, 1998).

Bogs are the only significant soil source of methane in the UK and may contribute around 120 kt methane/y. Other ecosystems are only occasional small sources of methane during prolonged wet periods. Soil as a source of methane is not included in the national atmospheric emission inventory.

Soil is not only a source of methane, but also a significant sink for methane and globally is estimated to oxidise 30 \pm 15 Tg y⁻¹ (Houghton *et al*, 2001). Methane oxidation is carried out by a group of aerobic microorganisms Largest methane (methanotrophs). oxidation rates occur in the upper aerobic layers of wetland soils (i.e. rice paddy fields, northern peat wetlands), where the methanotrophs oxidise a significant fraction of the methane produced by the methanogens living in the anaerobic, reducing environment in the deeper layers of wet soil. In drier ecosystems forests are the largest sink for methane. The main parameters affecting methane oxidation rates are soil disturbance, nitrogen additions and changes in bulk density, water content and diffusion properties and changes in soil temperature.

Fertilized and cultivated soils consume methane at rates of 40% or less of those in undisturbed forest soils as a result of complex short-term and long-term adverse effects of soil disturbance, causing shifts in microbial species diversity, and inhibition of methanotrophic activity by ammonium additions via fertilisation or nitrogen deposition (Hütsch, 2001, Smith *et al*, 2000). UK soils can oxidise between 17 and 36 kt $CH_4 y^{-1}$ and thereby sequester 14 - 30 % of the methane emitted from Britain's natural wetlands. However, the methane oxidation in soils balances less than 2% of the total annual anthropogenic and natural methane sources.

Carbon dioxide

Soils act as a very large store of carbon; globally, they hold three times as much carbon as the atmosphere. Table 2 shows that UK soils hold 4562 Tg of carbon, much of which is held in seminatural vegetation. Soils act as a sink for carbon dioxide if the input from plant litter exceeds the loss from decomposition or a source if this balance is reversed. In cool, wet climates, where decomposition is slow, carbon accumulates in the form of peat, which comprises 60 % of UK soil carbon. If the climate warms and dries, as predicted, this large store of carbon is vulnerable to being released, with a potential positive feedback loop being created as the additional carbon dioxide adds further to the climatic warming.

Recent work has suggested that carbon is generally being lost from UK soils, possibly at high rates (Bellamy et al, 2005), though the amount of climatic warming to date cannot account for the reported losses. Land use change is another possible explanation for this trend. Land use change has a major influence on the soil carbon balance, as the soil structure may be disturbed (e.g. by ploughing) and different vegetation types produce different quantities and qualities of litter. Globally, it is estimated that around 50 Pg C have been emitted to the atmosphere from soils, following conversion of natural, undisturbed land to cultivated.

Table 2. Distribution of soil carbon in the UK by land use category, from Bradley et al. (2005). Units are Tg of carbon in the top 100 cm.

	Semi-natural	Woodland	Pasture	Arable	Gardens	Total
England	310	108	686	583	54	1740
Scotland	1498	227	341	110	10	2187
Wales	121	45	162	8	3	340
N. Ireland	86	20	156	33	1	296
UK	2015	400	1345	734	69	4562

Land in other types (rock, bare, etc) and 'urban' are assumed to have zero carbon.

agricultural land (Paustian et a,. 2000).

Historically, conversion of semi-natural land to pasture and arable has been an important source of carbon dioxide in the UK. However, in recent years, with changing trends in agriculture and forestry, land use change has provided a net sink for carbon dioxide, largely because of reduced demand for cropland and the expansion of the forest area. Future trends in land use are hard to predict, but the UK is committed to submitting annual inventories of all greenhouse gas emissions and sequestration arising from land use change under the United Nations Framework Convention on Climate Change and the Kyoto Protocol.

Summary

In the UK, soils are a net emitter of 85 kt N₂O, 100 kt methane and are a sink for 1942 kt carbon dioxide. The three greenhouse gases differ in their global warming potential, due to different atmospheric lifetimes and radiative forcing (the ability to absorb solar radiation). Over a 100 year time horizon the global warming potential of nitrous oxide is 296 times and of methane 23 times larger than that of carbon dioxide. Taking these differences into account shows that UK soils emit nitrous oxide at a rate of 25,338 kt CO_2 equivalent y⁻¹ and methane at a net rate of 2140 kt CO_2 equivalent y⁻¹ and carbon dioxide at a net rate of -1942 kt CO_2 equivalent y⁻¹. Thus the net greenhouse gas emission from UK soils is 25,537 kt CO_2 equivalent y⁻¹, which is about 4% of the UK total annual greenhouse gas emission.

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UTE SKIBA and PETER LEVY

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Dr Ute Skiba is a specialist in the measurement of trace gas emissions from soils and is interested in understanding the processes and variables that control the fluxes. Dr Peter Levy is an ecosystem modeller, specialising in modelling carbon dioxide and other greenhouse gas fluxes. Some of their work at CEH feeds into the UK annual inventory of greenhouse gas emissions and equivalent European bodies. Projects of both scientists are supported by DEFRA, SEERAD, NERC and EU funds.

Meeting report

The 2006EnvironmentalChemistryGroupDistinguishedGuestLectureandSymposium

The impact of climate change on air quality was the title for this year's Environmental Chemistry Group Symposium, which incorporated the ECG's 2006 Distinguished Guest Lecture and was held at Burlington House on March 1st.

The symposium was opened by **Hugh Coe** (Manchester University) who spoke on *Aerosols, air quality and climate*. After sketching out the nature of the anthropogenic forcing of climate change, Dr Coe drew attention to the uncertainties which exist in our understanding of aerosols – both in relation to climate change and in terms of their immediate effects on health and habitat.

Aerosols cause around 10,000 premature deaths each year, and they are also responsible for acid deposition on poorly buffered soils and for nitrification of low-nutrient habitats. Current areas of atmospheric aerosol research, which are being vigorously investigated in response to demands for climate change predictions at a regional scale, include:

- the importance of the rate of growth (temporal decreases in number density matched by an increase in average particle mass);
- the nature of the organic matter associated with aerosols;
- and the role of the carbonaceous material present in aerosols.

Guang Zeng (University of Cambridge) talked on the *Global* modelling of chemistry and climate interactions. She described the use of the Meteorological Office's Unified Model 4.5 to develop a view of climate in 2100. Using predictions of:

temperature change;

•

- changes in vegetation (biogenic emissions);
- and increases in anthropogenic emissions in a scheme involving 60 reactive species in 170 gas phase photochemical reactions,

Guang has been able to predict changes in tropospheric ozone and nitrogen dioxide over the next hundred years.

Her work showed that the oxidising capacity of the atmosphere would change chiefly due to increased biogenic emissions (e.g. isoprene) and changes in relative humidity, but also linked to changes in soil-NO_x emissions. Changes in landatmosphere interactions were identified as significant and in need of further assessment and understanding.

This year's **Distinguished** Guest Lecture was given by Mike Pilling (University of Leeds) who was also the first recipient of the ECG DGL Medal. His lecture was entitled Climate change and air quality – a chemist's perspective. Prof. Pilling pointed out that even though substantial reductions in air pollution emissions had occurred since the 1970s (primary PM₁₀ and NO_x emissions have decreased), increasing attention was now being given to secondary PM₁₀ formation and long distance ozone transport and formation. For instance, emissions from the US cause an 0.5 ppb(v) a year increase in background ozone as measured at Mace Head.

There will also be important effects caused by predicted temperature increases on tropospheric pollution. Summer heat waves like those of 2003 will become the norm in 2040 (in 2003 there were1500 excess deaths in France of which 30% were due to air pollution).

Ultimately issues such as these can only be fully understood by establishing chemical mechanisms (MCMs: Master Chemical Mechanisms) with comprehensive kinetic data and by comparing simulated outputs with those from smog chambers and field measurements.

Simulations and predictions of the chemical effects of climate change require more precise and complete data from experimentalists for successful MCM modelling. For example, many organic compounds are conveyed into the free troposphere from the boundary layer by strong convective fronts. This transport requires the determination of rate constants over a large temperature range (down to 220 K). Such rate constants can be measured by laser flash photolysis. The 'hypothetical' reaction mechanisms can then be tested in smog chambers (e.g. the heavily instrumented chambers in Valencia), comparisons made to and field experiments.

In the case of transatlantic ozone transport, such field experiments were carried out by taking measurements from four aircraft flying along and across the New York ozone plume as part of a programme of "multiple interceptions of New York polluted air masses".

As far as understanding the chemistry of climate change is concerned, Prof. Pilling used the example of methane to illustrate the uncertainties that exist in predicting the effects of climate change on atmospheric methane concentrations – changes in the atmospheric oxidative capacity (atmospheric OH radical concentrations) are particularly salient and uncertain.

Prof. Pilling concluded his presentation by explaining the importance of isoprene chemistry as global temperature increases, and describing changes that may occur in PAN chemistry, which would affect PAN's role as a reservoir for nitrogen oxides.

This sequence of lectures provided an integrated and extensive overview of climate change chemistry. The speakers were expert and their expositions were given with great clarity. The capacity audience benefited from both these attributes.

Dr LEO SALTER

Air quality web sites

Alex Ledbrooke from the Air Quality Unit, Cornwall College reviews the features and scope of some of the UK's air quality web sites.

Government-related sites

Environment Agency – Environmental facts and figures, which provide an overview of the state of the environment of England and Wales. A labyrinthine site with various levels of information.

http://www.environmentagency.gov.uk/yourenv/eff/

Department for Environment Food and Rural Affairs (DEFRA) – A web site for local authorities and those working in the air quality field. The site contains all the documents needed for the Review and Assessment of local air quality in connection with the Air Quality Management Area (AQMA) declaration. But there are not many pages aimed at the non-specialist reader trying to understand what might be happening on his or her doorstep. The long lists of documents are sometimes difficult to find.

http://www.defra.gov.uk/environment/a irquality/index.htm#aqstrategy

Department of Health – Air Pollution

- The Department of Health offers a small section on air pollution and specifically on the negative health effects. The site has three sub-sections, which include air pollution publications and research into air pollution sponsored by the Department of Health, as well as a number of external links.

http://www.dh.gov.uk/PolicyAndGuida nce/HealthAndSocialCareTopics/AirPo llution/fs/en

Committee on the Medical Effects of Air Pollutants (COMEAP) – An advisory body for the Department of Health, the COMEAP site contains a number of expert reports and reviews which can be downloaded for free. Reports are archived by date, thus searching is fairly easy – if you know when the report was published. Otherwise the search engine will help you find reports using keywords.

http://www.advisorybodies.doh.gov.uk/ comeap/index.htm

Consortium sites

Care4Air – **South Yorkshire Clean Air Campaign** – If you live in South Yorkshire and have an interest in air quality, you will be well looked after on this site, and can be kept informed of news via the Care4AireZine.

http://www.care4air.org/index.shtml

City of York Council – Air Quality – The City of York takes its air quality seriously. An AQMA was declared in 2002 and there has clearly been a lot of work since. Each stage has been well described by well written reports which includes photos, maps etc. All the reports are available to download as pdf files, as are leaflets on how to reduce your contribution to air pollution.

http://www.york.gov.uk/environment/ai rquality/index.html

Doncaster Metropolitan Borough Council – Air Quality – Information on this site includes local action plans, real-time pollution concentrations, and personal health impacts. There is also a sister site, Fresh Air with similar information produced for young readers.



Monitoring airborne PM 10 (and PM2.5) has been a controversial subject for some time, as most automated monitors showed poor agreement with the European standard method without the need to apply 'correction' factors. However with the recent publication of a report by DEFRA the TEOM - FDMS has been shown to be equivalent to the European reference method <u>without the use of factors</u> across the whole of the UK. In addition the FDMS is the only monitor able to provide valuable data about the level of volatile and non volatile mass within the PM and with an optional accessory can also measure "black smoke" or carbon. FDMS is available as an upgrade to most existing TEOM monitors or as a complete replacement unit. Contact us for more information, a quotation, or with your existing TEOM serial number for upgrade advice.



T. 01452 849111

- E. enquire@airmonitors.co.uk
- W. www.airmonitors.co.uk

http://www.doncaster.gov.uk/airq/index .asp (Fresh Air)

Mayor of London – Air Quality – Information on personal health effects, sources of pollution, and the Mayor's Air Quality Strategy, which details schemes that aim to 'lead the way' on air quality issues.

http://www.london.gov.uk/mayor/envir onment/air_quality/index.jsp

The London Air Quality Network – This is an easy to navigate, interactive web site providing the user with up-to-date air quality data from monitors around the London boroughs. The site contains a wealth of information providing an ideal tool for students and amateur air quality enthusiasts alike.

http://www.londonair.org.uk/london/as p/home.asp

Welsh Air Quality – Web site of the Welsh Air Quality Forum – Another web site with interactive features including access to data and an alert to high air pollution. Users can learn about various pollutants, health impacts, read the latest News Letter, or visit a host of national and international links to related pages.

http://www.welshairquality.org.uk/

Equipment

Air Monitors – One of the leading firms in air quality monitoring technology, the Air Monitors site provides technical and other details of monitoring equipment.

http://www.airmonitors.co.uk/

Information/databases

Institute of Air Quality Management (**IAQM**) – the most prominent feature of the IAQM is the detailed mission statement giving a clear and concise description of the institutes aims and objectives. There are also dates of forthcoming events, job advertisements and an exclusive member's area. An interesting feature is the discussion forum where users are invited to post a question, though this useful facility seems underused. http://www.iaqm.co.uk/index.htm

Air Quality Management Resource Centre (AQMRC) – University of the West of England – This site includes information on events run by the Centre (and others), AQMAs in the UK, useful links on legislation, links to other organisations working within the air quality management field, and details of regional air quality groups in the South West.

http://www.uwe.ac.uk/aqm/centre/inde x.html

National Society for Clean Air (NSCA) – The NSCA offers much information, and the site is well constructed making it easy to find. The topics are diverse, with many links to external sites. There is also a list of forthcoming NSCA events.

http://www.nsca.org.uk/pages/index.cf m

World Health Organisation (WHO) – A search for 'air quality' in the WHO's search engine found proximately 11,800 matches! Amongst this bounty of information, the most useful sections include WHO air quality guidelines, an up-to-date list of reports, and the link to the AQ2.2 software download. If you're looking for health effects and air quality, look no further than this site.

http://www.euro.who.int/air

NETCEN – The UK National Air Quality Information Archive – The site contains statistics from the UK Automatic Urban Network with useful facilities for downloading selected data from all the monitors. The site also provides information about Local Air Quality Management including help for local authorities declaring AQMAs etc. http://www.airquality.co.uk/archive/ind ex.php

Encyclopaedia of the Atmospheric Environment – The Manchester Metropolitan University run this site and as the name suggests it includes a lot about the environment. A useful site for younger students or members of the public.

http://www.ace.mmu.ac.uk/eae/english. html **Air Pollution Information System** (**APIS**) – Searching the myriad of information on the APIS web site is geared around four main search categories; Pollutants; Impacts by Issue; Impacts by Ecosystem and Legislation and Agreements.

http://www.apis.ac.uk/index.html

Air Quality Management Magazine – Essential reading for anyone working in the air quality industry. This monthly magazine will keep you updated on research and project progress, new equipment and conference reports from around the UK and beyond. An informative and entertaining read.

http://www.air-qualitymanagement.co.uk/

UKAtmosphericDispersionModellingLiaisonCommittee(ADMLC) – Lack of an internal searchengine in this site meansscrolling upand down the pages to find information.http://www.admlc.org.uk/links.htm

Friends of the Earth – This site lacks a dedicated section on air quality. Using the search engine did reveal a list of press releases and articles, but these are not sorted into categories – making it difficult to search for something specific. Overall this is a disappointing web site at present.

http://www.foe.co.uk/index.html

Consultancy sites

Air Quality Consultants (AQC) – Major air quality consultants with many years experience. All the services offered are covered, as well as reports on previous projects and a list of current studies. The recent 'clients list' proves the popularity of AQC with large organisations – such as DEFRA, Tesco and the Highways Agency.

http://www.aqconsultants.co.uk/

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Meeting report

Coastline Management

 19^{th} January 2006, On the CoastNET conference Participatory planning and working with natural processes at the coast was held at the National Institute for Marine and Coastal Management (RIKZ) in The Hague. The meeting was partially funded by the Corepoint Project (EC Interreg 3BProgramme). Participants from (Royal consultancy firms Haskoning, Halcrow), international delegates (e.g. University of Athens, University of the Azores) and the UK (EA, DEFRA) attended the meeting. The Dutch hosts were also well-represented - reinforcing their county's innovative response changing coastal processes, to which are the consequences of climate change.

In his opening address, Lies Dekker gave the stark statistics that 60% of the Netherlands is below sea level and 80% of the GNP is generated from this area. Currently sand is being used to hold the 1990 coastline (12M m³ pa increasing to 30M m³ pa as sea level rises). These themes were developed by the next speaker (Niels Roode, RIKZ) who pointed out the complexities brought to flood defence strategies by the consequences of spatial planning, urbanisation, population growth and EC environmental legislation (http://www.comrisk.org/).

Subsequent speakers focused on:

Case studies: Alde and Ore 'A North Sea gem' (Bill Parker, the Alde and Ore Estuary Planning Partnership, Suffolk Coasts and Heaths Unit); Loe Pool (Leo Salter, Cornwall College); Coastal Flooding 2005: The Atlantic coastline of the Uists (William Richie, University of Aberdeen); GIS and ICZM – a case study for impacts visualisation (Helena Calado, Azores University); Working with natural processes: experiences from Irish beaches (John McKenna, University of Ulster); Changing national coastal policy through local engagement - a case study for North Norfolk (Jessica Milligan, Tyndall Centre, UEA).

General approaches: Challenges to reducing flood risk (David Collins, EA); Shareholder engagement in UK flood and coastal erosion risk management (Adam Hosking, Halcrow).

Engineering solutions: Planning and constructing a coastal protection scheme in Volos, Greece with the participation of the local community (Constoentinos Moutzouris, University of Athens); Coastal erosion problems in South Sicily (Giorgio Melfi, University of Cadiz); No 'one size fits all': a discussion of prominence, disguise and control in coastal engineering (Greg Guthrie, Royal Haskoning).

Choices were described as 'hold the line', 'no active intervention' or 'realignment to a more defendable line' and there was tension between those arguing for a more natural manipulation of the coastline and those who put forward hard engineering solutions. However, engineering solutions have been made an essential part of the equation when the socio-political consequences of a planned allowance of inundation are too high.

This makes the implementation of UK Shoreline Management Plans (SMP) difficult – especially when Local Authorities have to respond to dissension by local partnership and stakeholder groups. Such problems are exacerbated by the 'no recompense' policy of UK central government and also by the possibility of locally developed planning constraints in relation to flooding dangers being overridden by the ODPM.

Some well-placed criticisms of the use of computer models to justify the construction of engineered beach defences were made. Models have great difficulty in giving a quantitative assessment as to how beaches work. But their use continues, despite the lack of validation. Numerical modelling cannot provide accurate predictions partly because initial conditions cannot be measured, partly because systems complex, but also because are understanding is incomplete (a very similar situation to air quality modelling).

What does seem clear is that there is a degree of incoherence in the UK government's response to the effects of climate change on sea level and that the situation in the UK where a few thousand houses are at risk offers the possibility of more sustained and cost effective (and environmentally positive) solutions than those which are necessary in the Netherlands.

Dr LEO SALTER,

Cornwall College, Pool, Redruth, Cornwall Web link: CoastNET http://www.coastnet.org.uk/

Environmental Chemistry Group Bulletin: *January 2006* CORRECTION

The use of dried hyacinth roots to remove arsenic from surface water

In the first paragraph on page 14 of the printed version of the *ECG Bulletin* (January 2006 edition), the units for the guideline value for arsenic in drinking

water were incorrectly given as mg l^{-1} . The correct units are $\mu g \ l^{-1}$. The corrected two sentences from this paragraph should therefore read "The WHO guideline value for arsenic in drinking water is 10 $\mu g \ l^{-1}$ [3]. The US EPA recently approved new guidelines,

which will phase in a maximum contaminant level of $10 \ \mu g \ l^{-1}$ [4]."

This error has been corrected in the pdf version of the *ECG Bulletin* (January 2006 edition), which will appear on the *ECG Bulletins* section of the RSC homepage from July 2006 onwards.

The politics and practice of sustainable chemistry in the UK

The first German conference on Nachhaltige Chemie (Sustainable Chemistry) was held at the Evangelische Academie in Tutzing on the 30th and 31st of January 2006. Delegates representing industry, government, academia. policy. education and NGOs attended this meeting, which was sponsored by BASF, the University of Freiburg and Umweltbundesamt (the Federal Environment Agency). Dr Jeff Hardy, Manager of the RSC's Environment, Sustainable and Energy Forum (ESEF) gave the opening presentation and spoke about Green and sustainable chemistry in the UK: politics and practice.

The Royal Society of Chemistry and the 'green' environment

Three initiatives in recent years have strengthened the RSC's involvement in promoting green and sustainable chemistry.

Environment, Sustainability and Energy Forum

The RSC's Environment, Sustainability and Energy Forum (ESEF) [1] was formed in 2003 in order to support, manage and co-ordinate more effectively on behalf of the members, and in line with the RSC Charter, the various important activities that take place related to health and safety, environmental chemistry, toxicology, hazard management, green chemical technology, energy and sustainability.

Green Chemical Technology and the RSC

American chemists Prof. Paul Anastas and Prof. John Warner first coined the term green chemistry in the 1990's. The RSC has been involved in green chemical technology since 1998 when it funded the start-up of the UK Green Chemistry Network (GCN) whose hub is at the University of York (described in the following section).

The RSC launched the *Journal of Green Chemistry* [2] in 1999 and has also published a number of books with subjects relating to green chemical technology including technical

publications and books aimed at educating students [3].

The RSC has also run a portfolio of conferences that related to green chemical technologies over recent years including, "Green Chemistry: Sustainable Products and Processes" in 2001 which was the first everinternational conference on green chemical technology.

The Green Chemistry Network

The Green Chemistry Network [4] was launched by the Royal Society of Chemistry and is based within the Department of Chemistry at the University of York. The main aim of the GCN is to promote awareness and facilitate education, training and practice of Green Chemistry in industry, commerce, academia and schools. To achieve this aim GCN:

- Provides links to other organisations and government departments,
- Organises conferences/workshops and training courses,
- Provides educational material for universities and schools,
- Writes newsletters and books with close links to the Green Chemistry journal,
- Provides prizes and awards for companies and university researchers,
- Runs specific-themed projects targeting key areas and groups.

UK centres of green chemical technology excellence

There are a number of UK centres of research excellence in green chemical technology including the Clean Technology Centre at the University of Nottingham [5], the York Green Chemistry Group [6], the Queens University Ionic Liquid Laboratories [7], the University of Leicester [8], Imperial College London [9] and the University of Manchester [10].

Technology transfer in the UK

Crystal Faraday

Crystal Faraday [11] was launched in 2001 and has three hub partners, the

RSC, the Institution of Chemical Engineers (IChemE) and the Chemical Industries Association (CIA). Crystal Faraday is the UK's innovation centre for green chemical technology. Crystal Faraday aims to unite industry and academics in a common purpose: successful innovation through green chemical technology leading to a profitable, sustainable future. Crystal provides practical, expert support to companies facing critical challenges such as supply and regulation, and helps them to take advantage of new markets driven by sustainability. Crystal also helps academics and funders to focus on the most critical technical problems, including biological feedstocks, energy and atom efficiency.

Chemistry Innovation Knowledge Transfer Network

In February 2006 a new Chemistry Innovation Knowledge Transfer Network (CI KTN) was launched [12]. Three Faraday Partnerships (Crystal, Insight and Impact) are integrating with the CI KTN and the DTI has invested £4.7m in this venture over three years. The RSC will be acting as the host organisation for the CI KTN.

The CI KTN aims to make it easier for UK companies to innovate, and lower It will provide a single, risk. independent point of access to a huge of expert people range and organisations that can assist with large or small science, engineering or manufacturing changes in businesses. The network will identify key areas of technology that need developing and will help facilitate knowledge transfer and collaborative working between business and the science-base.

International Collaboration

There are a number of mechanisms through which the UK interacts with international green chemical technology stakeholders, including:

- Interaction between learned and professional bodies (such as between the RSC and GDCh);
- European (such as FPVI) and international research and exchange programmes (see section on SusChem below);

- Interaction between green chemical technology networks (such as between the GCN and the American green chemistry institute, GCI);
- Organising and attending international conferences (the RSC sponsors the international green and sustainable chemistry conference the next meeting is to be held in Delft in 2007);
- Exchanging educational best practice and sharing green chemical technology teaching materials.

EuropeanTechnologyPlatformforSustainableChemistry (SusChem)

SusChem seeks to boost chemistry and chemical engineering research, development and innovation in Europe [13]. SusChem's objectives are to:

- Maintain and strengthen the competitiveness of chemical industry in Europe based on technology leadership;
- Meet society's needs in close cooperation with all stakeholders;
- Boost and sustain chemistry research in Europe;
- Improve EU framework economic and regulatory conditions to inspire chemical innovation; and
- Contribute to Sustainable Development in Europe.

In addition a Horizontal Issues group is addressing barriers and constraints generic to EU chemistry innovation, such as research infrastructure and innovation framework conditions, which are cross-cutting and are best managed on a pan-platform level. The RSC is supporting the Horizontal Issues group.

Success stories and barriers to progress

It is encouraging to see that the examples of green chemistry are no longer limited to academia or to a few converted companies, but now the philosophy has been adopted by some much bigger organisations.

Marks and Spencer have replaced potentially harmful phthalates and alkyl phenol ethoxylates used in motif transfers and printed panels in children's' clothing and to launch a complete range of own-brand household cleaning products without the use of any synthetic cleaning ingredients or artificial colours.

Unique have developed a synthetic lubricant technology [14] that is now used in 500 million refrigeration compressors has contributed to:

- Reduction in energy consumption by up to 25%
- Simplification of compressor system design
- Reduction in noise levels by up to 50%
- Significant improvements in environmental quality
- Reduction of over 25 million tonnes carbon emissions.

However, whilst green chemical technology is making huge strides forward in many respects, there remain significant barriers to its widespread adoption and success, including:

- Financial constraints in the UK there is a significant funding gap between the proof of principle research stage and the construction of a working prototype or demonstration plant.
- Lack of time a number of UK companies need to employ all their resources just to maintain their market share; there is simply no time or resources to innovate or diversify into new products.
- Skills gaps green chemical technologies are often cutting edge and require new skills when compared to traditional chemical technologies.
- Knowledge gaps green chemical technologies are still being developed, and whilst knowledge in areas such as ionic liquids and renewable feedstocks is growing at a substantial rate, there are still significant knowledge gaps that require researching.
- **Mindset** green chemistry is still considered a fringe discipline by many and whilst some excellent examples exist where the adoption of its principles have resulted in significant cost reduction and increase in market share it is not yet widely seen as a mechanism for commercial success.

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The Royal Society of Chemistry

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Other topics discussed at the Nachhaltige Chemie Conference included: the criteria of sustainable chemistry; industrial applications for sustainable chemistry (including fuel additives and white biotechnology); chemical leasing; chemical education (including a project on sustainable organic chemistry featuring 70 practical experiments for undergraduate students see http://www.oc-praktikum.de/); innovation; sustainable design; and Corporate Social Responsibility.

References:

[1] www.rsc.org/ESEF

[2]

http://www.rsc.org/publishing/journals/ GC/Index.asp

[3]

http://www.rsc.org/Publishing/Books/in dex.asp

[4]

http://www.chemsoc.org/networks/gcn/

http://www.nottingham.ac.uk/supercriti cal/beta/

[6]

http://www.york.ac.uk/res/gcg/GCG/ho me.htm

[7] http://quill.qub.ac.uk/

[8] http://www.le.ac.uk/ch/greenchem/[9]

http://www3.imperial.ac.uk/chemistry/r esearch/researchsections/catalysis [10]

http://www.ceas.manchester.ac.uk/resea rch/researchthemes/

theenvironmentandsustainabletechnolo gy/

[11] http://www.crystalfaraday.org[12]

http://ktn.globalwatchonline.com/epice ntric portal/

site/menuitem.4a44a1cccbb4eea21ef52 110eb3e8a0c/

[13] www.suschem.org

[14] http://www.uniqema.com

Cornwall College, the Environment, and Loe Pool

Cornwall College often features in the pages of the *ECG Bulletin*, mainly as a result of the peripatetic efforts of its Research Director, Dr Leo Salter, and his colleagues. The participation of Cornwall College in the Coastline Management conference, mentioned elsewhere in this issue, is an excuse to reproduce another photograph of Loe Bar*, and is an opportunity to describe Cornwall College's environmental activities in more detail.

Cornwall College offers several Foundation Degrees with an environmental content and a BSc in Environmental Resource Management. Much of the project work associated with these courses is linked to the rural environment and often has a marine or aquatic theme. These projects and the staff who supervise them benefit the



Cornwall College, Camborne Campus

local authorities and NGOs in Cornwall, for whom demands are always greater than resources. Hence the College plays an important role for the region and the local communities by providing facilities, manpower resources a degree and of specialist expertise.

The College's contribution on Loe Pool at the Coastline Management conference (whose proceedings are summarised in this issue

summarised in this issue of the ECG Bulletin) reflected the conference's

ambitions to describe local solutions and good practice in the coastal zone. The paper presented at the meeting discussed the way in which Cornwall College brought together regulators and others who have statutory

responsibilities for the environment[†] to plan a long-term series of interventions for the management* of Loe Pool. By identifying



Loe Bar, Cornwall

financially achievable environmental targets, long-term cooperative action is being achieved. This is a flexible management solution, which maintains interest and focus on the Pool. But it also recognises the budgetary priorities of the various organisations.

*A detailed account of the Loe Pool Management Forum appeared in the July 2003 edition of the *ECG Bulletin* together with a photograph of Loe Pool and the shingle bar separating the lake from the sea.

[†] Environment Agency, English Nature, local and regional government, the owners of the site (National Trust), and the local water company (South West Water)

Forthcoming meetings for environmental scientists

The First International Environmental Best Practices Conference

Conference Centre, Olsztyn, Poland 7th to 10th August 2006, http://www.uwm.edu.pl/wosir/EBP/

Graduate Summer School in Atmospheric Measurement

Isle of Arran, Scotland 6th to 18th September 2006, www.see.leeds.ac.uk/ncas/ncas_summer/i ndex.htm

Renewable Resources and Biorefineries Conference

University of York, York 6th to 8th September 2006, http://www.rrbconference.net

NSCA Air Quality Committee

7th September, 2006, rpilling@nsca.org.uk

1st International IUPAC Conference on Green Sustainable Chemistry

Dresden University of Technology, Dresden, Germany 10th to 15th September 2006, www.gdch.de/vas/tagungen/tg/5559.htm

Second International Conference on Natural Aquatic Colloids and Nanoparticles

University of Plymouth, Plymouth 13th to 14th September 2006, www.gees.bham.ac.uk/research/aquanet

10th International Symposium on Environmental Radiochemical Analysis

The Randolph Hotel, Oxfordshire 13th to 15th September 2006, http://www.rsc.org/era2006

July 2006

Environmental Forensics: Chemical, Physical and Biological Methods

University of Durham 18th to 21st September 2006, http://www.rsc.org/EnvForen

Environmental Sustainability

Houldsworth Building, University of Leeds 5th October 2006, http://www.eee.leeds.ac.uk

International Conference on Pesticide Use in Developing Countries

Arusha Intenational Conference Center, Arusha, Tanzania 16th to 20th October 2006, http://www.ancap.org/ANCAP-SETAC.html

12th Symposium on Sample Handling for Environmental and Biological Analysis

Zaragoza University, Zaragoza, Spain 18th to 20th October, http://www.iaeac.ch

The Energy Review: An Analysis for UK Industry

Royal Society of Chemistry, London 9th November 2006, http://www.rsc.org/EnergySector/

International Conference & Exhibition on Green Industry

Gulf Hotel Bahrain (www.gulfhotelbahrain.com), Manama, Bahrain 20th to 22nd November 2006, http://www.green-industry.org

Coastal Futures Climate Change & the Marine Environment

30th November 2006, www.coastms.co.uk

World Wetlands Day Conference 2007

31st January to 1st February 2007, www.coastms.co.uk

Greenhouse Gases: Mitigation and Utilization

Queen's University, Kingston, Canada 8th July to 12th July 2007, http://www.chem.queensu.ca/greenhouse/

Resources at the RSC Library & Information Centre for the environmental scientist

New books and monographs

The following titles on environmental topics, toxicology, and health and safety were acquired by the Royal Society of Chemistry library, Burlington House, during the period January to June 2006.

Biodiesel: Growing a New Energy Economy

Pahl, G., Chelsea Green Publishing, White River Junction, Vt., 2005, ISBN/ISSN: 1931498652, Accession No: 20060022

Butyl Acetates

Copestake, P.; Malcolm, H., International Programme on Chemical Safety (IPCS): World Health Organisation (WHO), Geneva, 2005, ISBN/ISSN: 9241530642, Accession No: 20060159

Chemicals in the Environment: Assessing and Managing Risk

Hester, R. E.; Harrison, R. M. (eds.), Royal Society of Chemistry, Cambridge, 2006, ISBN/ISSN: 0854042067, Accession No: 20060128

Fundamental Toxicology

Duffus, J. H.; Worth, H. G. J. (eds.), Royal Society of Chemistry, Cambridge, 2006, ISBN/ISSN: 0854046143, Accession No: 20060132

Hexafluoropropylene

(ECETOC Joint Assessment of Commodity Chemicals No. 48)

Gribble, M. (ed.), European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), Brussels, 2006, ISBN/ISSN: 0773633948, Accession No: 20060155

Practical Environmental Analysis

2nd edition Radojevic, M.; Bashkin, V. N. (eds.), Royal Society of Chemistry, Cambridge, 2006, ISBN/ISSN: 0854046798, Accession No: 20060179

Risk Assessment of PBT Chemicals

Gribble, M. (ed.), European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), Brussels, 2006, Accession No: 20060153

1,1,1,2-Tetrafluoroethane (HFC-134a)

(ECETOC Joint Assessment of Commodity Chemicals No. 50) European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), Brussels, 2006, ISBN/ISSN: 0773633950, Accession No: 20060169

Tin and Organic Tin Compounds

(IPCS Concise International Chemical Assessment Document No. 65)

Howe, P.; Watts, P., World Health Organisation, Geneva, 2006, ISBN/ISSN: 9241530650, Accession No: 20060157

2,4,6-tribromophenol and Other Simple Brominated Phenols

(IPCS Concise International Chemical Assessment Document No. 66) Howe, P. D.; Malcolm, H. M., World Health Organization, Geneva, 2006, ISBN/ISSN: 9241530669, Accession No: 20060158

Water Contamination Emergencies: Enhancing Our Response

Gray, J.; Thompson, K. C. (eds.), Royal Society of Chemistry, Cambridge, 2006, ISBN/ISSN: 0854046585, Accession No: 20060161

RSC Virtual Library

Some titles on environmental and related topics for e-Books in the *NetLibrary* and Elsevier's *Referex Chem* collections of the RSC Virtual Library are shown below. RSC members are allowed remote access *via* a computer to the complete electronic contents of these books.

Titles from the NetLibrary Collection

Chemical Concepts in Pollutant Behavior (eBook)

Tinsley, I. J., J. Wiley, Hoboken, N.J., 2004

Chemical Consequences:

Environmental Mutagens, Scientist Activism, and the Rise of Genetic Toxicology (eBook)

Frickel, S., Rutgers University Press, New Brunswick, N.J., 2004

Environmental Analysis and Technology for the Refining Industry (eBook)

Speight, J. G., J. Wiley, Hoboken, N.J., 2005

Environmental Laboratory Exercises for Instrumental Analysis and Environmental Chemistry (eBook)

Dunnivant, F. M., J. Wiley, Hoboken, N.J., 2004

Environmental Organic Chemistry (eBook)

2nd edition Schwarzenbach, R. P. et al, J. Wiley, Hoboken, N.J., 2003

Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (eBook)

1st revised edition United Nations Publications, New York, 2005

Gulf War and Health: Updated Literature Review of Sarin (eBook)

National Academies Press, Washington, D.C., 2004

Health and Medicine: Challenges for the Chemical Sciences in the 21st Century (eBook)

National Academies Press, Washington, D.C., 2004

The Politics of GM Food: A Comparative Study of the UK, USA, and EU (eBook)

Routledge Research in Environmental Politics: 6

Toke, D., Taylor & Francis, London, 2004

Riegel's Handbook of Industrial Chemistry (eBook)

Riegel, E. *et al*, Kluwer Academic, New York, 2003

Riot Control Agents: Issues in Toxicology, Safety, and Health (eBook)

Olajos, E. *et al*, CRC Press, Boca Raton, Florida, 2004

A Small Dose of Toxicology: The Health Effects of Common Chemicals (eBook)

Gilbert, S. G., Taylor & Francis, Boca Raton, Florida, 2004

Soil and Water Chemistry: An Integrative Approach (eBook)

Essington, M. E., CRC Press, Boca Raton, Florida, 2004

Transforming Sustainability Strategy Into Action: The Chemical Industry (eBook)

Beloff, B. et al, J. Wiley, Hoboken, N.J., 2005

Wiley's Remediation Technologies Handbook: Major Contaminant Chemicals and Chemical Groups (eBook)

Lehr, J. H., J. Wiley, Hoboken, N.J., 2004

Titles from the Referex Chem Collection

Bretherick's Handbook of Reactive Chemical Hazards

6th edition Urben, Peter; Bretherick, Leslie, Elsevier Butterworth-Heinemann, 1999

Chemical Process Safety: Learning from Case Histories

Sanders, R. E., Elsevier Butterworth-Heinemann, 1999

Environmental Control in Petroleum Engineering

Reis, J. C., Elsevier Gulf, 1996

Environmental Engineering Weiner, R. *et al*, Elsevier Butterworth-Heinemann

Fundamentals of Air Pollution

Boubel, R. et al, Elsevier Academic Press, 1994

Handbook of Air Pollution Prevention and Control

Cheremisinoff, N. P., Elsevier Butterworth-Heinemann, 2002

Handbook of Hazardous Chemical Properties

Cheremisinoff, N. P., Elsevier Butterworth-Heinemann, 1999

Handbook of Water and Wastewater Treatment Technologies

Cheremisinoff, N. P., Elsevier Butterworth-Heinemann, 2001

Hazardous Waste Compliance

Florczak, C. *et al*, Elsevier Butterworth-Heinemann, 2001

Hazardous Waste Handbook

Lippitt, J. et al, Elsevier Butterworth-Heinemann, 2000

Industrial Waste Treatment Handbook

Woodard, F., Elsevier Butterworth-Heinemann, 2001

Lee's Loss Prevention in the Process Industries

2nd edition, volumes 1-3 Lees, F. P., Elsevier Butterworth-Heinemann, 1996

Pollution Prevention through Process Integration

El-Halwagi, M., Elsevier Academic Press, 1997