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Bulletin

RSC | Advancing the
Chemical Sciences

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CARBON DIOXIDE

1756: Joseph Black reports his studies of carbon dioxide, or 'air fixed' in magnesium alba (MgCO₃) that is released by heating. He found that this fixed air was also generated when chalk (CaCO₃) is treated with acid. Black tested the gas and found that it extinguished rather than supported flames and discovered that when

diffused into lime water (calcium hydroxide) the solution would turn cloudy. He also knew that it was denser than common air and demonstrated pouring the gas out of beakers onto flames to extinguish them. Black showed that the same 'fixed air' was produced by fermentation and respiration by demonstrating the clouding of lime water, a test still used in schools today.

2006: MEASUREMENT OF ATMOSPHERIC CARBON DIOXIDE: p. 2;
ATMOSPHERIC CARBON DIOXIDE AS A CHEMICAL FEEDSTOCK: p. 18.

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Joseph Black, *Experiments upon Magnesia Alba, Quick-lime, and other Alcaline Substances*, (Alembic Club Reprints No. 1), Clay, Edinburgh, 1893.

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The measurement of atmospheric carbon dioxide

There is a strong case for arguing that the accurate measurement of carbon dioxide in the atmosphere is the most important analytical challenge presented to contemporary chemistry. The initial uncertainties linking increased carbon dioxide levels to climate change voiced at the beginning of this century have been replaced by the economic and political realities of restricting our dependence on the combustion of fossil fuels, if we wish to avoid serious changes to the climate and to the environment. Key to the decisions that lie ahead in the next decade are the data on atmospheric carbon dioxide levels. **Paul Monks** from the University of Leicester, and an ECG committee member, describes his research group's collaboration in the measurement of atmospheric carbon dioxide using satellite-based analytical techniques.

ENVISAT

Retrieval of total columns of greenhouse gases with suitable accuracy and precision from space is a relatively new and challenging task. With the recent launch of the SCIAMACHY instrument on board the satellite ENVISAT (Figure 1), there is now an ability to measure the global total column amounts of a range of greenhouse gases (CO_2 , CH_4 and N_2O) [Buchwitz *et al.*, 2000; Buchwitz *et al.*, 2004].

In the near future, NASA will launch the Orbiting Carbon Observatory (OCO) [Crisp *et al.*, 2004], the first dedicated space-based CO_2 mission, that is expected to sample the CO_2

columns with adequate precision and accuracy for carbon budget estimates to be made.

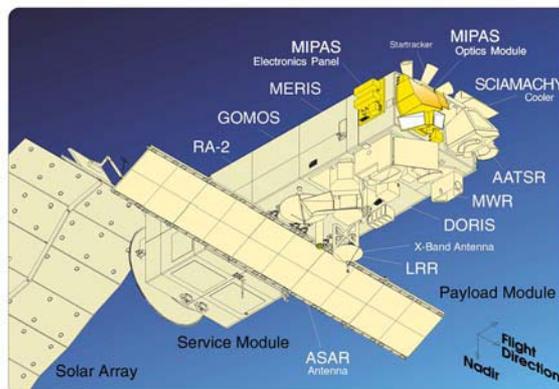


Figure 1: ENVISAT is an advanced Earth observation satellite with a unique combination of sensors to vastly improve the range and accuracy of scientific measurements of the atmosphere, oceans, land surface and ice. Its total range of capabilities far exceeds those of any previous Earth observation satellite. It was launched in spring 2002 by an Ariane-5 launcher.

Atmospheric carbon dioxide

Since the industrial era the atmospheric concentration of CO_2 has risen by $\approx 30\%$ from 280 (± 10 ppmv) to 367 ppmv in 2000 [IPCCC, 2001] with growth rates varying between 0.9 ppmv/yr and 2.8 ppmv/yr.

The increase of CO_2 in the atmosphere is caused by increased CO_2 emissions primarily due to fossil fuel burning ($\approx 75\%$) and changes in land use ($\approx 25\%$). Only about half of the emitted CO_2 remains in the atmosphere, where it affects the earth's radiation balance. The rest is partly dissolved in the oceans and partly taken up by the biosphere over land.

Measuring atmospheric carbon dioxide

Atmospheric measurements from the CO_2 surface network, consisting of about 100 stations, have been used to infer partitioning of CO_2 sources and sinks amongst oceans and land [e.g.

Bousquet *et al.*, 2000; Gurney *et al.*, 2002]. These studies showed that the land uptake of CO_2 , and ocean uptake to lesser extent, varies considerably in time and space. In the 1980s the land-atmosphere net flux was close to zero, mainly as a result of changes in land use (deforestation in the tropics), while during the 1990s the terrestrial ecosystem represented a strong sink comparable to the oceans [IPCCC, 2001].

More recent studies suggest that the oceans may have played a much larger role in the absorption of CO_2 [Sabine *et al.*, 2004]. The accuracy of these findings is, however, limited due to the low number of atmospheric and oceanic CO_2 measurement sites and the rather sparse distribution of them around the globe. In particular, the global networks lack continental stations that are representative of sources and sinks over vegetated areas. In addition, the temporal sampling of ground-based networks is too low. To predict future atmospheric CO_2 levels, more accurate quantification and understanding of the carbon sources and sinks is needed. In addition, verification of the Kyoto protocol, which aims at reducing anthropogenic emission of greenhouse gases, requires an accurate quantification and monitoring of CO_2 sources and sinks.

Satellite measurements, by their inherent spatial and temporal sampling, have the potential, if they can measure with suitable accuracy, to improve the greenhouse gas flux estimates derived from theoretical modelling, surface and airborne measurements. Combination with models through data assimilation and inverse modelling would be a particularly powerful method with which to take advantage of the new CO_2 data sets. In a supplementary article, which is available on the ECG page of the RSC's web site, I describe in more detail the methodology for satellite-based measurements of atmospheric carbon dioxide concentrations.

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- BIOGRAPHICAL NOTE:** Paul Monks' primary research interests are the scientific questions underlying: the role of photochemistry in the control of atmospheric composition; chemistry and transport, particularly the impact of long-range transport on chemical composition; the feedbacks between climate and atmospheric chemistry; organic complexity and the control of regional pollution and the measurement of the troposphere from space.
- An extended version of this article, *Measuring atmospheric CO₂ from space*, is available on the ECG page of the RSC's web site at <http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/bulletin.asp>

Interactions between air quality and climate change

Introduction

We constantly emit pollutants into the atmosphere from a wide range of activities, including transport, industry, power generation and heating our homes. Secondary pollutants are formed in the atmosphere by chemical reactions involving the primary emitted species. Some pollutants, such as CO₂, cause climate change and are known as greenhouse gases (GHGs), while others, e.g. NO₂, act locally, are injurious to health and are air quality pollutants.

Most emitting activities produce both greenhouse gases and air quality pollutants, so that limiting one type of pollutant could lead to decreases or even increases in the other type. For example, reducing SO₂ emissions from power stations reduces slightly the efficiency of generation and so leads to the emission of more CO₂ per kilowatt generated. At present there is little or no connection between the strategies and legislation we develop to limit climate change and to improve air quality. But the identification and promotion of win-win policies, those leading to synergistic emissions

reductions, and the identification and, if appropriate, elimination of win-lose policies, have clear advantages.

There is a further way in which climate change and air quality in the UK can interact. The weather conditions in the UK will alter as the climate changes. Hotter summers, especially if accompanied by stagnant air resulting from anticyclonic conditions, could increase the frequency of photochemical smog episodes. On the other hand it is predicted that winter time inversions, often accompanied by high concentrations of NO₂ and particulate matter, will be less frequent.

These issues were considered in a recent report by the Air Quality Expert Group that advises the Government and the Devolved Administrations on concentrations, sources and characteristics of air pollutants in the UK. This article is a selection from some of the more chemical aspects of that report.

Greenhouse gases and radiative forcing

The surface of the earth is warmed by absorption of light from the sun; heat is

lost by emission of infrared radiation, some of which is absorbed by greenhouse gases in the atmosphere. Increases in the concentrations of these gases, following the industrial revolution, has led to a slight rise in temperature that is predicted to increase further, by a few degrees Celsius, over the coming century. CO₂ is the most prevalent and effective GHG, but CH₄, N₂O and chlorofluorocarbons are also important.

Radiative forcing provides a measure of the effect of anthropogenically derived GHGs on radiation. Radiative forcing is defined as the change in the net radiation balance at the tropopause (the boundary between the troposphere and the stratosphere) caused by a particular human induced mechanism in the absence of any climate feedbacks. **Figure 1** shows a bar chart of radiative forcings from the Third assessment report of the Intergovernmental Panel on Climate Change [IPCC (2001)]. It shows the contributions from the four GHGs listed in the previous paragraph for the year 2000, relative to 1750, i.e. before the Industrial Revolution. It demonstrates that the contribution from CO₂ is indeed largest, but that the other GHGs also make a significant

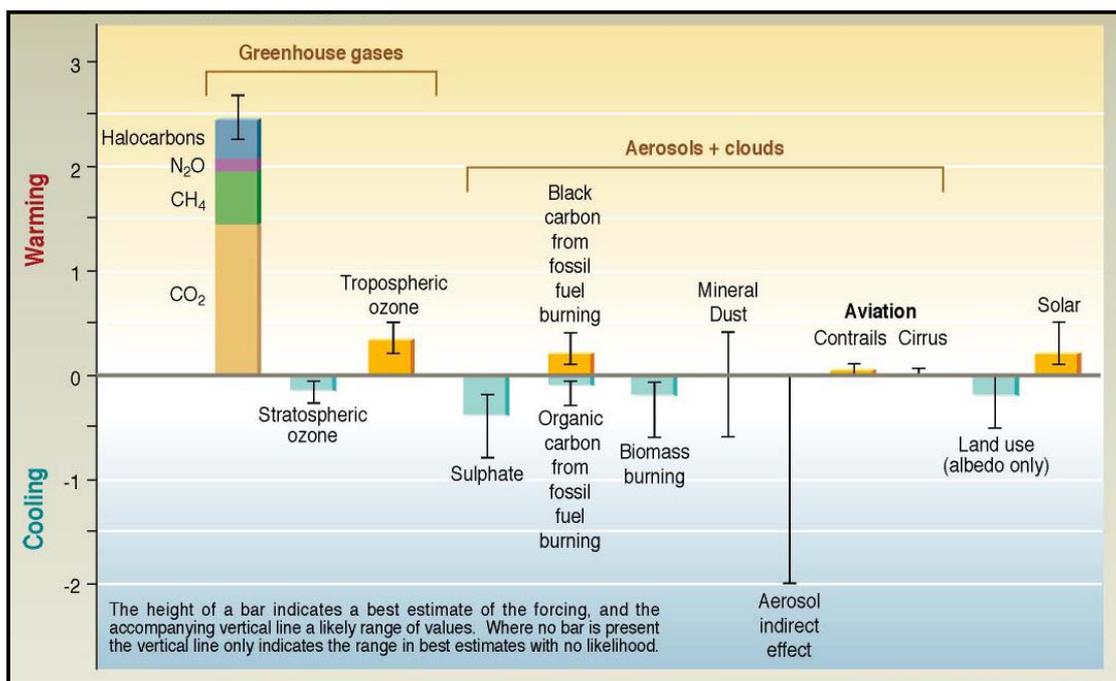
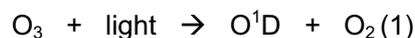


Figure 1: Anthropogenic and natural forcing (W/m^2) of the climate for the year 2000, relative to 1750. (IPCC, 2001)

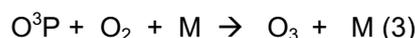
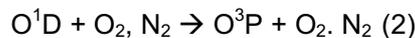
contribution. Water vapour absorbs IR radiation but is not included in **Figure 1** because it rapidly equilibrates with the surface of the earth, especially over the oceans, so that its atmospheric concentration is determined largely by temperature rather than emissions strengths. However, it does provide an important positive climate change feedback. As the temperature rises, its atmospheric concentration will increase with a consequent increase in its IR absorption.

Ozone formation in the troposphere – regional chemistry and photochemical smog formation

Figure 1 shows that ozone is also a GHG and provides a direct link with air quality. Ozone is a major target of air pollution mitigation strategies, because of its effects on respiration and on ecosystem health. It is a secondary pollutant, formed from reactions involving NO_x ($NO + NO_2$) and volatile organic compounds (VOCs), such as butane and ethene. The reactions are initiated by sunlight, *via* the photolysis of ozone to produce an excited electronic state of atomic oxygen, O^1D :



O^1D then is either deactivated on collision with O_2 or N_2 to form ground state oxygen, which reacts with O_2 to regenerate O_3 , or forms OH on reaction with H_2O :



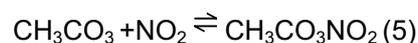
OH reacts with VOCs, either by H abstraction or addition, which is followed by reaction of the product radical with O_2 to form a peroxy radical, which in turn reacts with NO to form NO_2 . A sequence of reactions can then regenerate OH. A key step is the NO to NO_2 conversion, because this forms O_3 : photolysis of NO_2 leads to $NO + O^3P$ and the oxygen atoms then react via reaction (3). Thus, although the reaction sequence is initiated by ozone photolysis, its chain character ensures that there is net ozone production, provided there is sufficient NO to react with the peroxy radicals; at low NO_x , the peroxy radicals react with other peroxy radicals to terminate the chain. Under these conditions, the reaction sequence leads to net ozone consumption.

These reactions are responsible for the formation of photochemical smog, of

which ozone is a major constituent. The timescale of the process is determined by the timescale of the initial attack of OH on the VOC, which can take minutes to years, depending on the VOC. In consequence, photochemical smog formation is a regional phenomenon – the air is carried over large distances during the overall reaction time.

Ozone formation in the troposphere – global chemistry

The same sequence of reactions is also responsible for ozone formation on a global scale. Much of the atmosphere is relatively unpolluted and the most important reactant species on this scale are CH_4 and CO and a key issue is the availability of NO_x to ensure ozone formation. Sources in remote regions include lightning and soils but also transport of NO_x from polluted regions. This process is effected through the formation of peroxyacetyl nitrate (PAN). PAN is formed by reaction of NO_2 with the peroxyacetyl radical, itself a product of OH-induced H abstraction of acetaldehyde followed by further oxidation.



PAN is consumed mainly by decomposition [reverse of reaction (5)]. At the surface its lifetime is short (~1h), but if it is lofted into the troposphere, where T is lower, it lives for many days and can be transported into unpolluted regions. Descent to lower altitudes leads to decomposition and hence to NO_x formation.

This chemistry also affects the concentration and hence the radiative forcing of methane. CH_4 is removed from the atmosphere by reaction with OH; its concentration is determined by the rate of emission from the earth's surface, by both natural and anthropogenic sources, and its rate of reaction with OH. Thus changes in [OH] are reflected in the global average [CH_4] and hence in its impact on global warming. [OH] reflects what is termed the oxidising capacity of the atmosphere which depends on the chemistry forming OH, e.g. reaction (4), and that removing it, e.g. reactions with VOCs. The story is complicated because of the chain nature of the reactions – OH is regenerated following reaction with a VOC, provided NO_x is sufficiently high, but not too high otherwise OH reacts with NO_2 to form nitric acid, a termination reaction. Clearly [OH] depends on emissions of VOCs and of NO_x , another clear link between climate change and air quality chemistry.

Global chemistry in a changed climate

What will be the effect of increasing future temperatures on the global scale oxidation chemistry? This issue has been investigated by Stevenson *et al.* (2005) who used global models to investigate the effects of changes in both future emissions and temperature on a 30 year horizon. As noted above, increases in temperature lead to increases in water vapour which increases the rate of reaction (4) relative to that of reaction (2). In those regions of the atmosphere where NO_x is low, so that the oxidative chain length is short, this change in rates leads to a decrease in ozone especially over the oceans. In forested regions, this change can be more than offset by the increasing temperatures leading to increases in emissions of hydrocarbons, and especially isoprene, from vegetation, promoting ozone formation, provided NO_x is available. A further

important effect of increasing T is to increase the rate of reaction (5) and hence reduce the lifetime of PAN and limit its ability to transport NO_x into remote regions. The changes they found in [OH] and hence in the oxidising capacity of the atmosphere were complex and difficult to interpret. The most important regions for removal of CH_4 by reaction with OH are near the surface in the tropics. The rate of reaction is highest there, because of the higher temperature coupled with greater photochemical activity. They found increases in surface OH in the tropical northern hemisphere and decreases in the southern hemisphere.

Aerosols (particulate matter)

Aerosols or particulate matter (PM) provide an even more complex issue, relating air quality and climate change. Particulate matter has deleterious effects on respiration but has also been implicated in cardiovascular disease. It is the smaller particles (< 2.5 μm in diameter) that have the greatest impact on health. Composition may be significant, but results are ambiguous. PM is emitted from road transport in the form of soot and also material deriving from wear – of brakes, tyres and the road surface. Other sources include quarrying, sea salt and desert dust. Secondary PM is formed from reactions occurring in the atmosphere, for example the oxidation of SO_2 into sulphate or NO_x into nitrate and by the oxidation of organic compounds.

In cities such as London, the primary road emissions are an important, but not dominant source of PM – the secondary PM, which is produced on a regional scale by the oxidation chemistry discussed above for ozone formation, is also important.

Aerosols also influence climate, but in a different way from GHGs. Soot, an important contributor to primary traffic emissions, absorbs incoming radiation and so leads to warming. Reflective aerosols, such as sulphate, reflect radiation and lead to cooling. Their effect, though, depends on where they are located. Over dark surfaces, such as the oceans, which have a low albedo (reflectivity) and absorb most of the incident radiation, their effect is large. Over snow, though, which has a high

albedo, their effect is much reduced. In addition, aerosols play a role in cloud formation, and affect the properties of clouds; clouds play a major role in the radiative balance of the atmosphere.

Figure 1 shows the different contributions aerosols make to radiative forcing. The *indirect effect* is that related to their role in cloud formation. The error bars in the Figure show that, in assessing the effects of anthropogenic emissions on radiation, aerosols provide the greatest uncertainty by far. The consensus is that the overall effect is negative (leads to cooling).

The cooling effects of sulphate aerosols led to the proposal by Crutzen (2006), that we should promote the formation of sulphate aerosol by burning H_2S in the stratosphere to reduce the effects of GHGs. Such an approach is a high risk strategy and presumes that we can assess fully the impacts of such an action – our understanding of the atmosphere is, however, not perfect. Crutzen himself stresses that it is a last ditch strategy and should not be a substitute for the more prudent approach of emissions reduction.

Global warming potential

The lifetimes of emitted species in the atmosphere affect their impact on climate change. This effect is usually incorporated into assessments via the global warming potential (GWP) which provides a measure of the relative potential impact of emissions of a particular substance upon global climate. GWPs are defined as the ratio of the time integrated radiative forcing from the instantaneous release of 1 kg of a trace substance relative to that for a reference gas, normally CO_2 . The timescale chosen is usually 100 years. The atmospheric lifetime of CO_2 is ~150 years and so, once emitted, it persists much longer in the atmosphere than methane, which has a lifetime of ~12 years. Methane, though, is a more effective absorber of infrared radiation and has a GWP of 23. The GWP for CO_2 by definition is 1. Aerosols have a lifetime that depends on their size but is typically only ~1 week. It is, therefore, difficult to calculate a meaningful GWP for them.

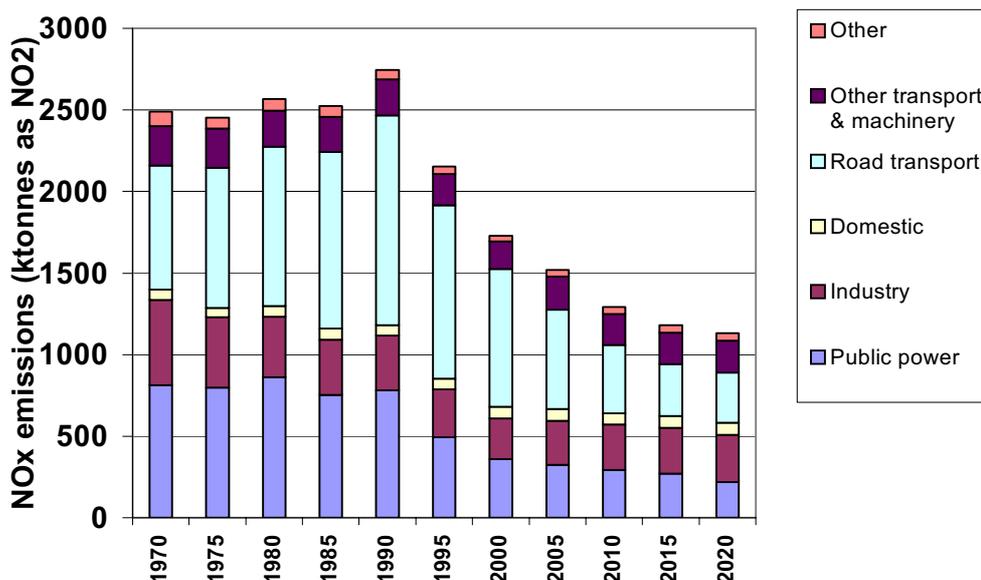


Figure 2: UK NO_x emissions by source, including predictions to 2020. (From Nitrogen Dioxide in the United Kingdom, First report of the Air Quality Expert Group, Defra, 2004).

A potential problem that has been identified, though, is that reducing the concentration of aerosols in the troposphere, in order to improve air quality, could lead to warming of ~ 1 °C (Brasseur and Roeckner, 2005), because of the reduction in the aerosol cooling effect.

Air quality in a changed climate

What effect will changes in climate have on air quality in the UK? Predictions are bound to be highly uncertain. Uncertainties in regional climate predictions are even greater than those for the global climate and it is difficult to predict future emission any further ahead than $\sim 10 - 20$ years. **Figure 2** shows the decrease in NO_x emissions in the UK since 1970. They show a sharp decrease in the 1990s, largely related to improved NO_x reduction technology in power stations and the fitting of three-way catalysts to cars. A decrease is predicted to continue out to 2020, but no estimates are available beyond then. Future changes in both emissions legislation and technology can lead to significant changes in the slopes of emissions vs. time graphs.

August 2003 gave a possible taste of likely effects, with present day

emissions. The high temperatures and stagnant air led to a serious photochemical smog episode, with elevated concentrations of both ozone and PM. Excess deaths during this short period in the UK were ~ 2000 , of which about one third were cause by poor air quality, the rest by the more direct effects of elevated temperature. Under the anticyclonic conditions experienced, the VOCs and NO_x required for smog formation were transported from the continent, but there was an additional source of the elevated ozone. Vegetation emits isoprene which had a very short lifetime of only ~ 20 minutes under the conditions that applied and so travelled only short distances from its sources in the still air (wind speed ~ 1 m s⁻¹). In the presence of the NO_x transported from mainland Europe, the isoprene was a significant source of ozone in the afternoons. Vegetative emissions of isoprene depend strongly on temperature and the concentrations of isoprene were much higher than is normally experienced in the UK because the temperatures were unusually high (high 30s °C). It has been predicted, on the basis of climate models, that more than half of all European summers are likely to be warmer than that of 2003 by the 2040s.

Linking climate change and air quality policies

It has long been said that climate change is the greatest threat facing mankind. At long last, the political climate is changing and it is increasingly accepted that emissions leading to climate change should be controlled as soon as possible. **Figure 1** demonstrates that it is not just CO₂ that should concern us. There are significant effects of other GHGs, and aerosols too may present a major problem. The latter effects are difficult currently to quantify, but could lead to enhanced global warming as air quality is improved.

It is likely that a wide range of approaches will be adopted to reduce CO₂ emissions, though we will, no doubt, remain dependent on combustion technologies over the coming decades. It is important that we do not simply press on with CO₂ reduction strategies without considering the wider implications for emissions of other GHGs, of aerosols and of the impact on air quality.

The strong linkage between emissions responsible for air pollution and those implicated in climate change demands a closer alignment of air quality and climate change policies. This is not currently the case. One problem is that

it is difficult to obtain the necessary information to make such an integrated environmental impact assessment. For example although it is generally accepted, on a g CO₂ emitted / km travelled, that diesel vehicles are more fuel efficient than petrol vehicles, this assessment does not take into account, for example, energy consumption differences in the refinement process. A full fuel cycle analysis is needed to make a reliable comparison. Furthermore, it is difficult to combine assessments of CO₂ impacts, with those of PM emissions on climate or of PM and NO_x emissions on air quality. Further work is urgently required to allow more robust assessments upon which to base future policies.

Acknowledgements

I am grateful to members of the Air Quality Expert Group on whose work

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This article is based in part on a presentation by Professor Pilling at the ECG's DGL and Symposium 2006. Colour versions of the Figures in this article may be seen on the ECG page of the RSC's web site at <http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/bulletin.asp>

Climate change, methane and ozone

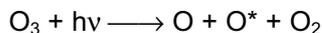
Introduction

Methane (CH₄) and tropospheric ozone (O₃) are the two most important trace gases involved in global warming, after carbon dioxide (CO₂). The concentrations of both of these gases have risen substantially during the industrial era, owing to the extraction and combustion of fossil fuels (IPCC, 2001). Their levels in the troposphere are closely linked via chemical reactions involving water vapour, and changes in the concentration of one will affect the concentrations of the other (Johnson *et al.*, 2001, 2002). Oxidation of methane is responsible for the majority of the ozone formation in the troposphere (West and Fiore, 2005). Production of the hydroxyl radical (OH), which is responsible for almost all the oxidation of methane in the troposphere, is controlled by the levels of ozone. In this article, the feedbacks between methane and ozone will be explained, and the impacts of climate change via water vapour levels will be discussed.

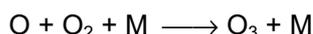
Ozone photochemistry

Ozone is photolysed by light at wavelengths smaller than 370 nm to produce an oxygen molecule and an oxygen atom. The latter may be

produced in two forms, a ground state (O) or an energetically excited state (O*). At wavelengths less than 310 nm, most of the oxygen atoms are in the excited state (Wayne, 1985).



The ground-state oxygen atom will react with oxygen molecules to regenerate ozone,

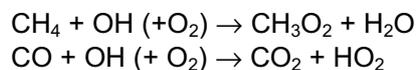


where M represents a third body (typically an oxygen or nitrogen molecule). The excited oxygen atom may either be quenched back to the ground state via collisions with a third body, or it may react with water vapour to produce two hydroxyl radicals,



Hydroxyl radicals are of fundamental importance in the chemistry of the troposphere. They react with almost all emitted pollutants, and such a reaction is the first step in the oxidation of pollutants. Taking the simplest hydrocarbon, methane, oxidation produces the intermediate species formaldehyde (HCHO) and then carbon monoxide. Carbon monoxide is oxidised exclusively by hydroxyl

radicals to form carbon dioxide. The initial step for methane is shown below, together with the reaction between hydroxyl radicals and carbon monoxide:



The methylperoxy radical (CH₃O₂) reacts further to produce formaldehyde, HCHO. The subsequent reactions of formaldehyde and hydroperoxy radicals (HO₂) will reform the hydroxyl radical. The oxidation of methane and carbon monoxide is therefore catalytic, as no net destruction of hydroxyl radicals occurs (Wayne, 1985).

Impacts of climate change on methane

The concentration of water vapour in the troposphere is controlled by a number of complex processes. In the lowest part of the troposphere, called the boundary layer, the mass of water vapour tends to increase with increasing temperature. Outside of the boundary layer, water vapour levels are controlled by many different physical processes. An increase in temperature may not lead to more water vapour in this region. However, overall, climate models tend to predict greater water

vapour levels in the troposphere with increasing temperature.

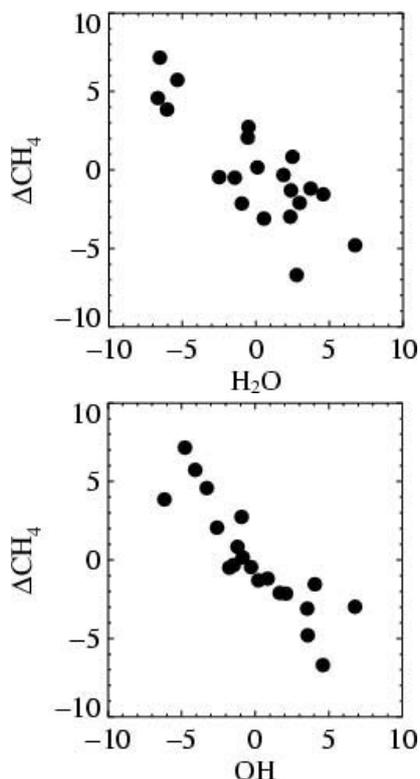


Figure 1: Scatterplots of the change in global mean methane concentrations with global water mass and global mean OH levels. The data have been detrended and scaled so that they lie on the same axes. The units are arbitrary.

If water vapour levels rise, the production of hydroxyl radicals from the excited state oxygen atom (O^*) is likely to increase. The oxidation rates of methane and carbon monoxide will also proceed more quickly, owing to the higher production rate of hydroxyl radicals. To investigate this feedback, a chemistry model was coupled to the Hadley Centre's climate model HadCM3. Levels of carbon dioxide were increased according to the IPCC SRES A2 emissions scenario (IPCC, 2000). This coupled chemistry-climate model was integrated forward in time. Scatter plots of the change in global mean methane levels against total atmospheric water vapour and global mean hydroxyl radical levels are shown in **Figure 1** for the first 20 years of the simulation. In both cases, a significant correlation exists between the change in methane levels, and each of the water vapour amount and hydroxyl radical concentrations. A similar plot using

global mean surface temperature (not shown) showed a distinctly poorer correlation. These results show that the level of water vapour in the troposphere exerts an important influence on the methane lifetime, via the production of the hydroxyl radical. As the climate continues to warm, this loss rate is likely to increase further. Overall, climate change results in greater production of hydroxyl radicals, and reduces levels of methane via increases in water vapour. However, this reduction is not enough to offset increased emissions from anthropogenic activities. By 2030, the reduction in methane levels owing to climate change effects is only 1 – 2%. For 2050, the methane levels are only 4% smaller when climate change effects are included (Johnson *et al.*, 2001).

Future ozone levels

Ozone levels in the troposphere have risen substantially since pre-industrial times (Volz and Kley, 1988), and have continued to rise in more recent times (Vingarzan, 2004). This rise in ozone levels is caused by increased emissions of precursor gases, such as nitrogen oxides (NO_x), carbon monoxide and hydrocarbons (Dentener *et al.*, 2005, 2006). In the future, as the climate continues to warm, the chemical reactions involved in producing ozone will proceed more quickly. If emissions of precursors also increase, ozone levels in the future will be even larger. However, owing to the increased water vapour in a future climate, surface ozone levels at least will be partly reduced via the reactions of the excited oxygen atom with water vapour, as discussed above (Johnson *et al.*, 2001; Stevenson *et al.*, 2006).

The competing effects of climate change and emissions increases on projected surface ozone levels for the year 2030 have been studied using a coupled chemistry-climate model. Three simulations were used: First, a control simulation (1) which used climate data and emissions suitable for the year 2000. The second simulation (2) used projected emissions for the year 2030, but the climate data for the year 2000. The third simulation (3) used projected emissions and a climate for the year 2030. The difference between the ozone levels from the

second and third simulations will illustrate the impact of climate change alone on projected surface ozone levels. The emissions were taken from the IIASA Current Legislation scenario (Dentener *et al.*, 2005). This scenario assumes the majority of countries will have implemented regulations requiring reductions in emissions of pollutants by 2030. These results are shown in **Figure 2**.

The top panel of **Figure 2** shows projected changes in annual mean surface ozone levels owing to increased emissions of pollutants only (Simulation 2 – Simulation 1). Ozone levels have only risen slightly over much of Europe and North America, by between 1 and 2 ppb, owing to the assumed reductions in emission in the Current Legislation scenario. The rise in ozone levels is slightly greater over Africa, by 2 – 3 ppb. The largest increases under the scenario occur over India and south-east Asia, by up to 15 ppb. This large increase in ozone levels over this part of Asia is due to projected increases in emissions of primary pollutants from power generation and vehicle numbers.

The same change in surface ozone levels, but also including the effects of climate change, are shown in the middle panel of **Figure 2** (Simulation 3 – Simulation 1). The patterns of change in the ozone levels are broadly similar to the top panel, with the largest increases once more over India and south-east Asia, and smaller increases over the continents in the northern hemisphere. However, the absolute increases in the ozone levels are smaller, and in some parts of the northern hemisphere ozone levels have decreased slightly, by 1 – 2 ppb. The inclusion of climate change has therefore decreased the projected surface ozone levels for 2030. The effect of climate change alone is shown in the lower panel of **Figure 2**. This panel is the difference between the upper and middle panels. Surface ozone levels have fallen by 1 – 2 ppb over most of the globe, although a rise of 1 – 2 ppb is predicted over parts of the Pacific Ocean. These results show that, as indicated above, climate change has generally decreased projected global surface ozone levels for 2030.

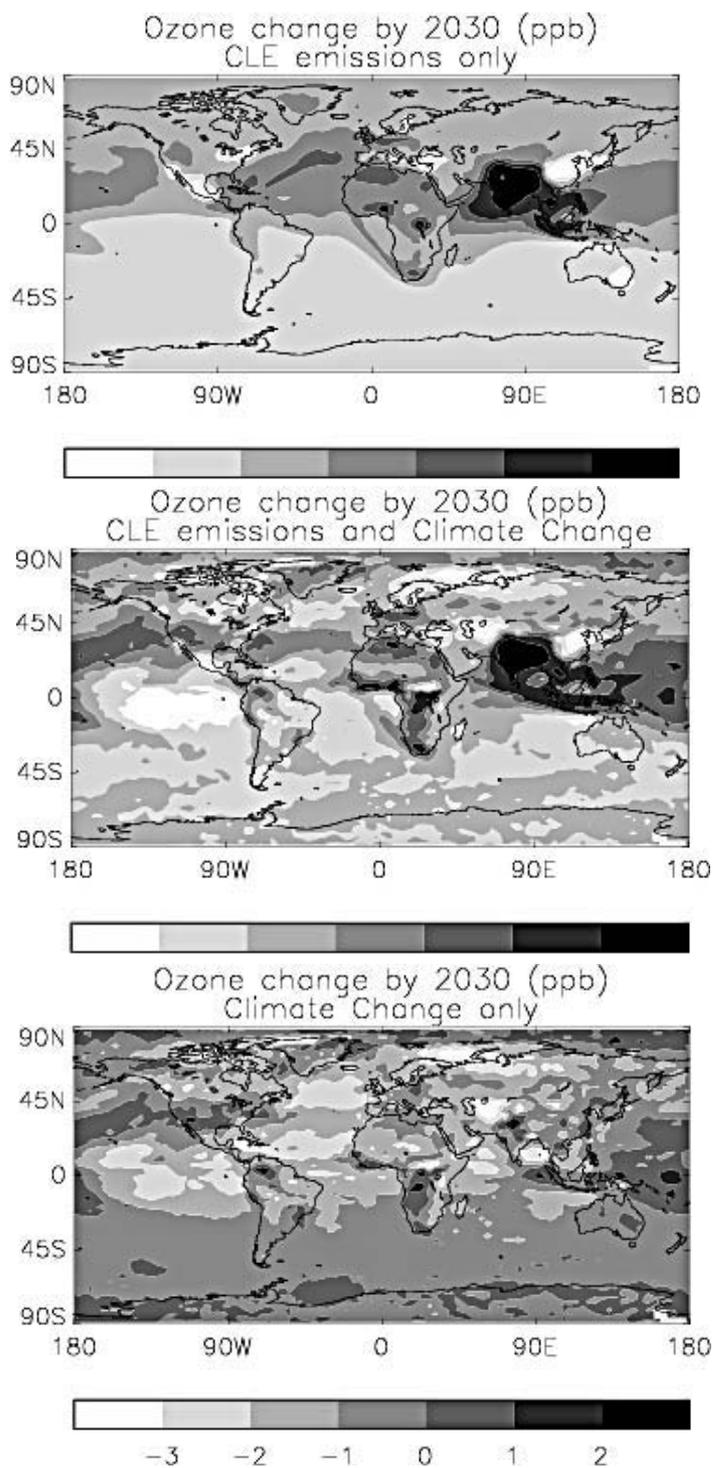


Figure 2: Projected change in annual mean surface ozone levels between 2000 and 2030, using estimated emissions for 2000, and the Current Legislation (CLE) emissions scenario for 2030. The top panel shows changes due to emissions increases alone. The middle panel illustrates the changes due to emissions increases and climate change. In both cases, a positive value indicates that ozone levels are greater in 2030 than 2000. The lower panel is the difference between the top and middle panels, and demonstrates the effect of climate change alone. A negative value indicates that climate change has reduced the projected ozone levels for 2030. The ozone differences are in shown in units of parts-per-billion (ppb) in all cases.

Summary

The levels of methane and ozone in the troposphere are closely linked via chemical reactions involving water vapour. Experiments using a coupled chemistry-climate model have shown that global methane levels are correlated with global water vapour levels, and global OH levels. Larger water vapour levels result in increased production of OH levels, and consequently smaller methane levels.

Further simulations using the coupled chemistry-climate model were used to study the effect of climate change on projected surface ozone levels for the year 2030. The water vapour levels are larger in the 2030 climate than in the 2000 climate. Climate change has reduced the projected ozone levels by 1 – 2 ppb over most of the globe. This reduction is due to the reaction between water vapour and excited state oxygen atoms. Owing to the increased water vapour levels, more excited state oxygen atoms react with water vapour, and fewer are quenched to the ground state to reform ozone. Hence, more hydroxyl radicals (OH) are made at the expense of ozone molecules, and ozone levels fall.

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Calculated tropospheric ozone changes between 2000 and 2100: the impact of climate change

Introduction

Tropospheric ozone (O_3) has been a focus for tropospheric chemical research both as a regional pollutant and as an important trace gas. High ozone levels are considered harmful to human health and vegetation. Ozone is a precursor of the hydroxyl radical (OH), which plays a key role in the oxidizing capacity of the atmosphere. Ozone is also important because of its greenhouse warming potential; it currently ranks as the third most important anthropogenic greenhouse gas after CO_2 and CH_4 .

Since pre-industrial times, anthropogenic activities have changed the chemical composition of the atmosphere considerably. Increasing surface emissions of methane (CH_4), carbon monoxide (CO), volatile organic compounds (VOCs) and nitrogen oxides (NO_x), produced by biomass burning and fossil-fuel combustion, have caused tropospheric O_3 concentrations to increase significantly (Volz and Kley, 1988).

The total amount of tropospheric O_3 is estimated to have increased by 30% globally since 1750, as reported in the Intergovernmental Panel on Climate Change (IPCC) (Houghton *et al.*, 2001). In a response to a continuing increase of surface emissions, a further increase of tropospheric O_3 is anticipated. In a changed future climate, tropospheric chemistry is

likely to be perturbed. In this article we report on the computed changes of O_3 between 2000 and 2100 based on the assumption of increases of precursor emissions, and explore the potential impact of climate change on tropospheric O_3 .

Chemistry-climate modelling

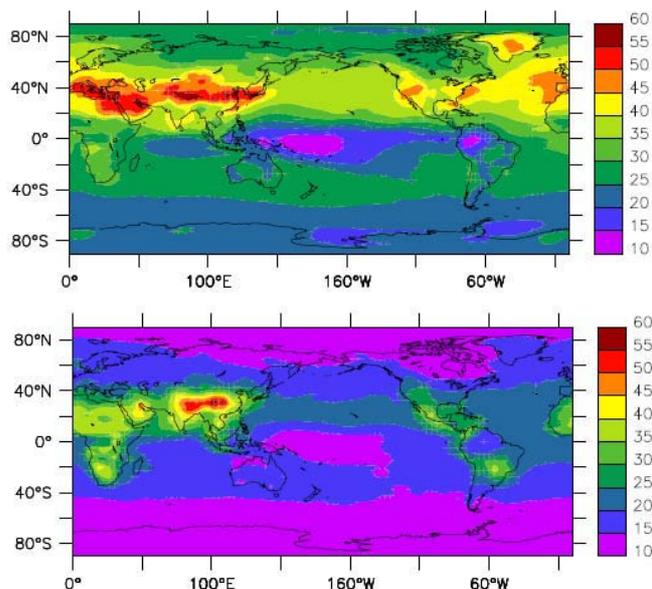
Tropospheric O_3 is formed as a secondary photochemical product of the oxidation of CO and hydrocarbons in the presence of NO_x . Its short chemical lifetime results in an inhomogeneous distribution and a stronger dependence on changes in trace gas emissions than other well mixed greenhouse gases. Due to the highly complex O_3 chemistry in the troposphere, it therefore requires a comprehensive chemical mechanism describing NO_x -CO- CH_4 -VOC chemistry to be incorporated in three-dimensional chemistry/climate models to accurately model the global O_3 distribution and to assess climate feedbacks.

To address this topic, we incorporate a detailed tropospheric chemical module into the U.K. Met Office (UKMO) climate model, the Unified Model (UM). Briefly, the UM was developed and used at the UKMO for weather prediction and climate research (Cullen, 1993). Here we use the atmosphere-only version (HadAM3) and the model's meteorology is forced using

prescribed sea surface temperatures (SSTs). It uses a hybrid sigma-pressure vertical coordinate, and the model domain extends from the surface up to 4.6 hPa. The tropospheric chemical mechanism includes 60 chemical species describing NO_x -CO- CH_4 -NMHCs chemistry. (NMHC; non-methane hydrocarbons). Chemical integrations are performed using an implicit time integration scheme. The model includes dry and wet deposition of trace species. There is no explicit stratospheric chemistry in the model, therefore daily concentrations of O_3 , NO_y , and CH_4 are prescribed at the top model layers, to produce a realistic annual cycle of these species in the stratosphere.

Calculated O_3 changes between 2000 and 2100

The model includes seasonally varying emissions of O_3 precursors. The data set are largely based on the IPCC Special Report on Emission Scenarios (SRES) for the years 2000 and 2100 (Nakićenović *et al.*, 2000), which makes assumptions on population growth and economic and technological development. We choose the SRES A2 scenario, which predicts relatively large emission increases, in order to assess the most pessimistic influence on future air quality. Under this scenario, the annual total CO emission increases from 1077 Tg in 2000 to 2327 Tg in 2100; and the annual total NO_x emission increases from 49 to 124 Tg



Figures 1a & 1b: Annual mean surface O_3 for year 2000 (a) (upper panel) and ΔO_3 (2100-2000) due to anthropogenic emission changes (b) (lower panel). Units in ppbv.

(N). Here, we investigate potential future ozone changes from anthropogenic emission changes, changes in meteorology, and climate change induced natural emission changes of isoprene and soil- NO_x . We assume twice present-day CO_2 loadings to represent a future climate (2100).

Figure 1a shows that modelled annual mean surface O_3 for 2000 varies between 40-50 ppbv over large parts of Europe, Asia and North America as a direct result of emissions of O_3 precursors. The background O_3 levels are from 15 ppbv to 25 ppbv with the year-round low values in Central Pacific Ocean. Tropospheric O_3 is not only produced in the source regions of its precursors but it is also transported to remote oceanic regions under favourable meteorological conditions. For example, the elevated O_3 levels in the northern Pacific Ocean are the result of transport of pollutants from Asia.

Figure 1b shows changes in surface O_3 between 2000 and 2100 assuming only changes in anthropogenic emissions, i.e. with unchanged climate. The background O_3 levels are calculated to increase 10-15 ppbv by the end of this century based on the A2 emission scenario. In the Northern Hemisphere (NH), over 30 ppbv of O_3 increases are calculated over polluted continents. The

largest annual averaged O_3 increases (over 40 ppbv) occur in Asia. The peak ozone concentration is calculated to reach 50 ppbv in summer months. For these regions, rapid economic growth and a population increase are predicted and can lead to an unacceptable air quality.

Increased surface emissions of O_3 precursors not only contribute to O_3 formation in source regions but also increased O_3 levels in remote regions through long-range transport. Vertical profiles of tropospheric O_3 in the year 2000 and the ΔO_3 (2100-2000) are shown in **Figures 2a & 2b**. The Figures show the propagation of chemically produced O_3 from the lower troposphere to the upper troposphere. The largest absolute increase of O_3 is in the upper troposphere between 20-40 °N where O_3 has a longer chemical lifetime and there is no surface deposition. Note that O_3 in this region has a high climate sensitivity, i.e. a larger contribution to radiative forcing to lower temperatures in the upper troposphere. There is a 75% increase in total tropospheric O_3 burden as a result of increased anthropogenic emissions.

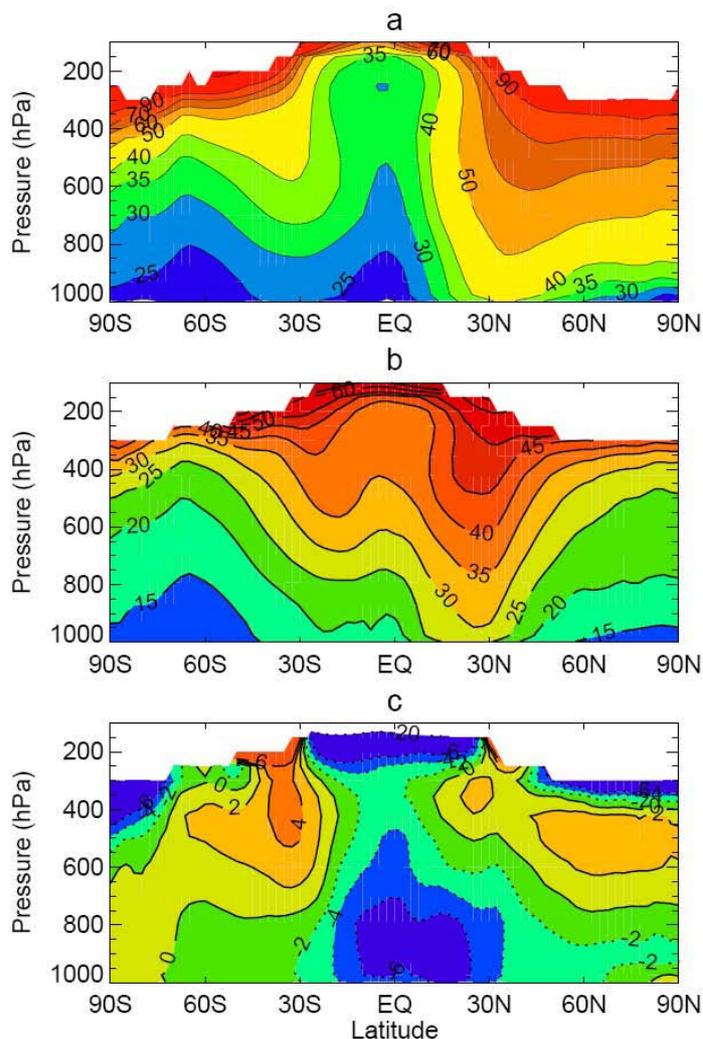
Impact of climate change

Changes in meteorology can affect the O_3 distribution by modifying both chemistry and transport. **Figure 2c**

shows O_3 changes due only to changes in meteorology. Feedbacks from climate change may have both positive or negative signs. Indeed, increased water vapour promotes chemical destruction especially in the tropical lower and middle troposphere, following photolysis of O_3 and the subsequent reaction of $O(^1D)$ with water vapour.

However, there are substantial increases of O_3 in the lower stratosphere, which propagate to the mid-latitude troposphere. In an anticipated warmer and wetter future climate, convection lifts more rapidly O_3 -poor air upwards in the tropics; a strengthened Brewer-Dobson circulation transports more O_3 -rich air into high latitudes. This leads to an O_3 reduction in the upper tropical troposphere and an O_3 build-up at high latitudes in the lower stratosphere and transports into the troposphere through enhanced stratosphere-troposphere exchange (STE). Calculations show that STE increases ~80% in a doubled CO_2 future climate (Zeng and Pyle, 2003) compared with the present-day climate. In summary, future climate change have both negative and positive impact on O_3 changes through intensified chemical destruction and enhanced stratosphere-troposphere exchange respectively. With climate change included, the overall feedback from the change in meteorology is slightly negative in this calculation (69% increase of tropospheric O_3 burden compared to 2000).

In a changed climate biogenic emissions are likely to change. For example, elevated CO_2 concentrations and increased temperature and humidity will contribute to increased emissions of isoprene from vegetation and of nitrogen species from the soil. Current estimates indicate that isoprene emissions are likely to increase by 50-80% in a double- CO_2 climate. We have adopted 50% increase in our experiment. Results show that increased isoprene emissions have little impact on the total tropospheric ozone burden. However, the spatial distribution of ozone is modified; ozone generally increases in the northern hemisphere throughout the model domain and decreases in the equatorial and southern subtropical regions.



Figures 2a, 2b & 2c: Annual and zonal mean tropospheric O_3 profile for 2000 (a); ΔO_3 (2100-2000) due to anthropogenic emission changes (b); and ΔO_3 due to climate change only (c). Units in ppbv.

Ozone destruction in the source regions is associated with increased ozonolysis by isoprene; this signal then propagates to higher altitudes. On the other hand, we obtain elevated ozone concentrations away from the emitting source regions and in downwind remote regions (e.g. the Indian and the Atlantic Oceans). Here, increased peroxy radicals from the degradation of isoprene contribute to ozone production in the NO_x -rich environment. In remote regions, PAN chemistry plays an important role in ozone formation; PAN can transport NO_x away from its source regions and contribute to ozone production in low NO_x environments. We have performed a sensitivity test by increasing NO_x emissions from the soil by 100% in the 2100 calculation, in line with available estimates. The result

shows that increased soil NO_x has a substantial positive feedback to tropospheric ozone (we achieve a 3% increase of the tropospheric burden). Further work needs to be carried out based on more accurate input of soil- NO_x emissions for the future climate.

Summary

We calculated tropospheric O_3 changes between 2000 and 2100 based on the most pessimistic emission scenario predicted for the year 2100. The calculations show a large increase in ozone in response to increases of O_3 precursor emissions, which is detrimental to the air quality. Climate change plays a significant role in modifying O_3 and the oxidizing

capacity of the atmosphere through both changes in circulation and perturbations in chemistry. Rigid emission control is urgently needed to improve air quality and to combat climate change.

Acknowledgement

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This article is based on a presentation by Dr Zeng at the ECG's DGL and Symposium 2006. Colour versions of the Figures in this article may be seen on the ECG page of the RSC's web site at
<http://www.rsc.org/Membership/Networking/InterestGroups/Environmental/bulletin.asp>

More on atmospheric hydroxyl radicals

A note from **Dwayne Heard** on the *commentary* by P. O. Wennberg, "Radicals follow the Sun", *Nature*, 13th July 2006, vol. 442, p. 145 and the *paper* by F. Rohrer and H. Berresheim, "Strong correlation between levels of tropospheric hydroxyl radicals and solar ultraviolet radiation", *Nature*, 13th July 2006, vol. 442, p. 184.

The hydroxyl radical, OH, is the atmosphere's detergent, removing unwanted emissions and controlling the concentration of almost all trace gases. It has a short lifetime in the atmosphere, less than a second, and its concentration is extremely small (less than 1 part in 10^{13} mixing ratio), yet it is important to measure, as OH embodies the ability of the atmosphere to process emissions. There has been a worldwide effort by a handful of groups to measure absolute concentrations of OH, with instruments developed over the last 15-20 years [1].

One instrument, based on laser-induced fluorescence spectroscopy at low-pressure (FAGE), has been developed at the University of Leeds. The major advances in our understanding of the chemistry of the atmosphere have resulted from comparing the field measurements of OH (made at a given location over a given time-period) with the output of numerical models, which themselves are constrained by co-measurements of the longer-lived trace species which produce and destroy OH. Comparisons have been made for remote sites where the air is very clean and free of man's influence, and relatively few chemical reactions are required to adequately describe the observed OH behaviour, and also in heavily polluted urban areas where the chemistry is highly complex and is dominated by man's emissions. In between is a gamut of scenarios of intermediate pollution with influences from biogenic and anthropogenic emissions.

In a paper published in *Nature* earlier this year [2], which was accompanied by a short commentary [3], OH measurements were reported from a field-campaign in the black forest at Hohenpeissenberg in Southern Germany, which lasted 5 years. What is unique about this study is the duration of the measurements, as normally measurements are only made for 1-2 months at a given location, and even less for aircraft measurements. Of particular interest is whether there was any observed trend in the level of OH over these 5 years, and hence any change in the ability of the atmosphere to look after itself. No such trend was observed, but the extensive data-set allowed a striking conclusion to be reached, namely that the OH concentrations, on average, were controlled by a single parameter, despite the fact that many reactions at this site are expected to control OH. The parameter is related to the sunlight intensity, specifically the rate at which one of the O-O bonds in ozone is broken to generate molecular oxygen and an excited oxygen atom, $O(^1D)$. The parameter is called $J(O^1D)$. A strong correlation between OH concentrations and $J(O^1D)$ has been observed before [1], as the reaction of $O(^1D)$ with water vapour is the major source of OH. However, what is surprising here is that the composition of the local environment, which might be expected to change during a seasonal cycle in Southern Germany, does not influence this strong correlation. The correlation with $J(O^1D)$ was also seen to be better than the correlation with a calculation of OH from a detailed model which includes all the chemistry producing and destroying OH!

As highlighted by Wennberg in his commentary on this work [3], we must not read too much into this strong correlation, as other controlling factors may cancel each other throughout the year. We can think about the concentration of OH being analogous to the level of water in a bathtub with the plug partly removed. The level is controlled by the rate of input from the taps, and the rate of output through the plughole. If we turn on more water, the level will rise, if we expose more of the plughole, the level will fall. The level, or OH concentration, is said to be in

steady-state and is a balance of sources and sinks. At Hohenpeissenberg, the rate of removal of OH is approximately the same all year round, although the nature of the sinks changes dramatically. In summer OH is removed more by biogenic hydrocarbons (highest emissions in summer) whereas in winter more so by CO and NO₂ (which peak in winter). For processes generating OH, the levels of $O(^1D)$ (sunlight) and water vapour are highest in summer, whereas another source of OH from reactions of nitric oxide, NO, are highest in winter (more NO).

In conclusion, although this work suggests that OH only depends on a parameter related to sunlight intensity (implying that OH instrument operators may retire!), the results at Hohenpeissenberg are most likely a balancing out of controlling factors. Also, the quantitative details of the correlation, i.e. how much OH is present for a given value of $J(O^1D)$, is strongly dependent upon geographical location, and cannot be predicted in advance. Finally, significant levels of OH have been observed at night in urban and forested areas, when there is no sunlight. In order to understand fully the ability of the atmosphere to cleanse itself, and to understand the complex effects of man's emissions and climate change on the atmosphere, we must continue to make OH measurements in all environments from the Poles to the Tropics.

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DWAYNE HEARD

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December 2006
<http://www.chem.leeds.ac.uk/People/Hheard.html>

Forthcoming symposium

Environmental Chemistry in the Polar Regions

11.45 Professor Tim Jickells, UEA
Productivity in Antarctic waters

Royal Society of Chemistry Environmental Chemistry Group

12.30 **Environmental Chemistry Group Annual General Meeting and lunch**

2007 Distinguished Guest Lecture & Symposium

13.15 Dr Anna Jones, British Antarctic Survey
Tropospheric chemistry in the polar regions

A **one-day** meeting to be held in the Council Room at the Royal Society of Chemistry, Burlington House, on **Tuesday 6th March 2007**, from 10:30 am onwards.

14.00 Professor Dwayne Heard, University of Leeds
Free-radical chemistry at high latitudes

The 2007 ECG Distinguished Guest Lecturer will be **Dr Eric Wolff** (British Antarctic Survey)

14.45 Coffee/tea

Symposium & Distinguished Guest Lecture

15.00 Introduction to the 2007 Distinguished Guest Lecture and presentation of the ECG DGL Medal

Environmental Chemistry in the Polar Regions

15.05 **2007 RSC Environmental Chemistry Group Distinguished Guest Lecture:**

Dr Eric Wolff, British Antarctic Survey
Frozen in time: the chemistry of polar ice cores

PROGRAMME

10.30 Coffee/tea and registration

11.00 Chairman's Introduction, Dr Brendan Keely (Chairman, RSC Environmental Chemistry Group)

16.05 Open Forum

11.05 Dr Brendan Keely, University of York
Sediment records of environmental change in Antarctica during the last 10,000 Years

16.30 Close

Coffee/tea will be served at 10.30 and 14.45.

A buffet lunch will be served at 12.45

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 (address below). Members of the Environmental Chemistry Group may also register by email. 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. 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.



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

The nearest Tube stations are Green Park and Piccadilly Circus.

ROYAL SOCIETY OF CHEMISTRY, ENVIRONMENTAL CHEMISTRY GROUP

Thirty-fourth Annual General Meeting, 6 March 2007 and Distinguished Guest Lecture & Symposium on *Environmental Chemistry in the Polar Regions*

Please tick the item(s) below as appropriate,

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Name:

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

Royal Society of Chemistry Environmental Chemistry Group

2007 Distinguished Guest Lecture & Symposium

Environmental Chemistry in the Polar Regions

A **one-day** meeting to be held in the Council Room at the Royal Society of Chemistry, Burlington House, on Tuesday 6th March 2007

Abstracts and biographical details of the speakers

Sediment records of environmental change in Antarctica during the last 10,000 Years

Dr Brendan J. Keely, University of York

Lake sediments contain a wide range of organic residues originating from the organisms that inhabited the water column at the time the sediments were deposited. Depth profiles of variations in the nature and distributions of these organic residues reflect changes in the populations of aquatic organisms in response to changes in environmental conditions. Derivatives of chlorophyll pigments are especially sensitive markers of the various different organisms that comprised the primary producer community. In addition, the pigments undergo a variety of different chemical modifications during cellular disruption and sedimentation, leading to structures that are diagnostic of particular environmental conditions. Low altitude lakes are particularly susceptible to environmental pressures and can provide detailed records of change over the duration of a lake's history. The talk will illustrate how organic residues in lake sediments have revealed changes in relative sea level, in the relative extent of primary production and in the extent of sulfur cycling in the Antarctic during the last 10,000 years.

Brendan Keely is a Reader in Chemistry at the University of York, UK, where he heads an active research

group within the Analytical Science and Environmental Chemistry section. After obtaining a joint honours degree in Chemistry and Geology at the University of St Andrews, Scotland, he moved to the University of Bristol where he obtained a PhD in Organic Geochemistry under the supervision of Professor James Maxwell FRS. This was followed by two periods of postdoctoral research at Bristol before being appointed to a lectureship at York in 1993. Current research interests centre on the development and application of mass spectrometry methods in organic geochemistry, pesticide analysis, forensics and scientific archaeology. Brendan is an associate editor of the journal *Organic Geochemistry* and Chair of the Environmental Chemistry Group.

Productivity in Antarctic waters

Dr Tim Jickells, University of East Anglia

The Southern Ocean represents a vast ocean area which has historically been heavily exploited, for instance by the whaling industry. However, in large parts of the Southern Ocean primary production by marine phytoplankton is low due to limitations in the supply of the key nutrient iron. I will briefly consider the nature and role of iron supply and contrast it with the supply of other nutrients (e.g. nitrate, silicon and phosphorus) in this area. I will also consider the effects of iron limitation on the biological community and the resultant feedbacks to atmospheric CO₂ uptake by the ocean in this area, and hence to climate. Finally I will present results from some recent studies in Antarctic coastal waters where iron limitation appears to be relieved by supply from glacial erosion and productivity is very high.

Tim Jickells graduated with a BSc (Hons) in Chemistry with subsidiary geology from Reading and then with an MSc in Oceanography from Southampton. He then went to work for the Clyde River Purification Board (now part of SEPA) in East Kilbride Glasgow as an assistant marine chemist. He then moved to Bermuda working initially on coastal pollution

issues and later concentrating on work offshore on the role of atmospheric inputs in regulating surface water biogeochemistry. He moved to Norwich in 1985 to take up a lectureship at UEA in the School of Environmental Sciences where he is now a Professor and Director of the Laboratory for Global Marine and Atmospheric Chemistry. His main research interests are on the role of atmospheric inputs on the biogeochemistry of the oceans and on nutrient cycling in coastal waters.

Tropospheric chemistry in the polar regions

Dr Anna Jones, British Antarctic Survey

Until recently, the snow and ice covered regions of the world received little interest from the atmospheric chemistry community. However, a number of field programmes in the Arctic and Antarctic have revealed many unexpected and interesting phenomena. The discovery of ozone depletion events within the polar marine boundary layer, for example, came as a complete surprise. We now know that tropospheric ozone depletion occurs both in the Arctic and the Antarctic. In the Arctic marine boundary layer in springtime, depletion can extend from the ground up to ~1.5km, with ozone concentrations dropping to near zero. In other studies it has been shown that the polar cryosphere can have a major influence on the overlying atmosphere. Rather than being inert, snow is highly photochemically active, with snowpack impurities photolysed to release reactive trace gases into the boundary layer. Since the initial discovery of NO_x production within the Greenland snowpack evidence for the production and release of a range of trace gases has been found. These processes appear to be ubiquitous, occurring wherever sunlight shines on snow. In the remote high latitudes of Antarctica and central Greenland, emissions from the snow dominate boundary layer chemistry. In this talk, I will describe these phenomena and present the latest findings from the polar regions.

Dr Anna Jones completed a numerical modelling PhD at Cambridge University before joining the British Antarctic Survey (BAS) in 1992. Dr Jones' initial research with BAS focussed on the stratosphere, but some years ago she moved closer to the ground to study boundary layer chemistry and exchanges between the air and the snow. Two seasons of field work have been completed in Antarctica, at the German research station, Neumayer, studying nitrogen chemistry and the production of NO_x from Antarctic snow. Dr Jones has recently taken part as a Principal Investigator in the CHABLIS project (the Chemistry of the Antarctic Boundary Layer and the Interface with Snow), in Antarctica, where the longest duration and most extensive atmospheric chemistry measurement campaign yet in coastal Antarctica has been conducted. For the past seven years she has run the Atmospheric Chemistry projects at BAS, involving laboratory and field experiments to further the understanding of clean air chemistry and air/snow exchange.

Free-radical chemistry at high latitudes

Professor Dwayne Heard,
University of Leeds

Free-radicals are ideal target species for chemical models of the atmosphere. They have short lifetimes (seconds) and their concentrations are therefore governed only by local *in situ* chemistry and not by transport processes. For example, the hydroxyl radical, OH, is responsible for the oxidative removal of the majority of trace gases emitted into the atmosphere, and hence is intimately involved in the control of greenhouse gas concentrations and the generation of secondary pollutants. 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. However, recent fieldwork has revealed elevated levels of free-radicals (e.g. OH, HO₂, RO₂, IO, BrO) demonstrating

the potential for significant processing. In this talk, I will describe measurements of free-radicals in the polar atmospheres of both hemispheres, and discuss what has been learnt about the chemistry of these regions from comparisons with model calculations.

Dwayne Heard received his undergraduate degree in Chemistry and D. Phil in gas phase kinetics and photochemistry from the University of Oxford. He was then a postdoctoral fellow at SRI International in Menlo Park, California, where he worked mainly on combustion diagnostics in flames, before moving to a lectureship at Macquarie University, Australia. He moved to the University of Leeds in 1994 as a Royal Society University Research Fellow, and is now Professor of Atmospheric Chemistry. His main research interests are field measurements of free-radicals in the atmosphere and the kinetics and photochemistry of atmospheric processes. His group has developed field instrumentation for ground and airborne platforms and has participated in field campaigns worldwide. He was formerly Chairman of the Royal Society of Chemistry Gas Kinetics Group (2004-5), and he has recently edited a book, *Analytical Techniques for Atmospheric Measurement*, which was published by Blackwell in 2006.

Frozen in time: the chemistry of polar ice cores

Dr Eric Wolff, British Antarctic Survey

Greenland and Antarctic ice cores contain a unique archive of the history of Earth's climate and atmosphere. The information exists principally in the chemical content of the ice: the isotopic proportions of the water, the chemicals trapped in snowfall, and the contents of the air bubbles that form as the ice is compressed. A huge range of analyses, some at ultra-trace levels, is used to extract the information. In this lecture, I will describe some of the major results obtained from ice cores in recent years. For example, it is only through

ice cores that we can be sure how the CO₂ content of the atmosphere rose above its natural range between about 1800 and the start of regular direct atmospheric measurements in the 1950s. From Greenland ice cores, we have seen that very abrupt changes in climate (occurring within a human lifetime) were a feature of cold climates. Finally, I will concentrate particularly on results from the European Project for Ice Coring in Antarctica (EPICA), which has recently extended our ice records back 800,000 years, and shown how the different components of the Earth System behaved over glacial-interglacial cycles.

Eric Wolff is a Principal Investigator at the British Antarctic Survey (BAS), where he leads the programme "Climate and Chemistry". This programme studies past climate using Antarctic records, and also studies the chemistry of the Antarctic lower atmosphere, in part to understand how ice core records are formed. After graduating in chemistry from Cambridge, Dr Wolff has spent most of his career at the BAS in Cambridge, interspersed with six Antarctic and two Greenland field seasons. He has studied several aspects of Antarctic ice, including the changing lead content of ice, the chemical causes of the electrical conductivity of ice, and the locations of impurities within the ice structure. His main focus now is on the use of ice cores to understand past climate and the behaviour of the Earth System. He has played a prominent role in major European ice core projects in Greenland and Antarctica, and now chairs the science group of the European Project for Ice Coring in Antarctica (EPICA), which has produced the longest records of climate and trace gases from ice cores, spanning some 800,000 years. Within EPICA, Dr Wolff has been particularly involved with aerosol chemistry in ice, making new interpretations of how components such as dust and sea salt relate to important environmental parameters such as sea ice.

Fenceline monitoring: perils and pitfalls

Heightened awareness of environmental issues has led to an increased urgency in tackling problem areas of pollution. Fenceline monitoring is a technique for alerting industry about these problems. **Dr Kim Hampton** explains.

Introduction

New and existing environmental legislation coupled with a greater sense of corporate responsibility can assist in the protection of the environment. For UK industry, the most far reaching (and relevant) legislation to date is the regulatory framework within **Integrated Pollution Prevention and Control (IPPC)**. IPPC is aimed at protecting the environment as a whole, taking into account emissions to air, water and land. The regulators, who are either the Environment Agency or a local authority depending on the activity, set permit conditions, i.e. the amounts of chemicals that are allowed to be released into the environment. These conditions are based in part on the implementation of Best Available Techniques (BAT), where the cost to the operator is balanced against the benefits to the environment.

The aim of IPPC is to prevent emissions and waste production, or at the very least reduce them to acceptable levels. If it is not practical to eliminate all the emissions to the environment, there is a need to monitor them to ensure permit levels are not exceeded. IPPC tends to be enforced at the exit point i.e. at the stack or effluent outlet. However, there are many emissions that cannot be tracked in this way, hence the need for **fenceline monitoring**. When fenceline monitoring is undertaken correctly, it is invaluable in assessing the gaseous pollutant emissions of a plant to the surrounding area.

A comprehensive monitoring scheme also influences the public perception of industrial plants. A plant which is seen to be monitoring for pollutants helps to instil public confidence, as well as

complying with IPPC and other legislative criteria such as local air quality regulations.

Fenceline monitoring: objectives

The primary objectives of effective fenceline monitoring are to:

- Evaluate the effectiveness of emission controls that are in place
- Evaluate air quality at the fenceline in terms of public health
- Develop site-specific protocols to ensure the air quality objectives and consent levels are not exceeded
- Ensure the data collected are of good quality and validated
- Provide information on risk management and information to the public
- Reduce the liability of the site owner.

How to carry out fenceline monitoring

Dispersion modelling

In order to carry out successful fenceline monitoring, a site has to be evaluated for its local climate, emission sources, and plant geometry. Any monitoring that is carried out is highly dependent on these factors and not just on the emissions themselves.

The best way of siting instrumentation is to carry out an initial dispersion modelling of a site. A recent EU funded project run by Sira Ltd., UK, evaluated different types of remote optical sensing open path instrumentation before use on industrial sites. The sites were modelled using computational fluid dynamic (CFD) modelling. The aim of the study was to compare the instruments as well as to provide data about pollutant emissions.

Instrumentation for fenceline monitoring

The instrumentation available for fenceline monitoring can be roughly

divided into two types – **point measurements** and **remote sensing open path optical instrumentation**. Both have their advantages and disadvantages, and selection is based on what is to be measured, the levels that are likely to be encountered and what the site operator wants from the data. There is no “one size fits all”.

The main advantage of **point measurements** is that the instruments are portable and easy to calibrate. However, to obtain any spatial information, multiple point sensors are needed. An incorrectly positioned point sensor will fail to detect the pollutant. Continuous monitors are available, or time integrated samples can be taken and then subsequently analysed in the laboratory.

With **remote sensing optical open path systems**, if the light beam path is broken by a pollutant, it will be detected. Hence a much greater spatial area can be covered and there is less likelihood that the pollutant plume will not be detected. Commercial systems monitor continuously but these instruments tend to be fixed, and they need to be carefully aligned in order to obtain valid data.

Apart from measuring pollutants, meteorological data (particularly wind speed and direction) need to be collected to check where emissions are coming from. In a highly industrialised area it is always possible that pollutants are entering a site as well as being emitted from that site.

Case study

A good example of how fenceline monitoring has been used to allay public fears and show that pollutant emissions are within limits is at the ConocoPhillips-Rodeo oil refinery, 25 miles north east of San Francisco. The monitoring system was installed as a result of releases from the refinery that impacted the surrounding community. A monitoring network was installed, made up of remote sensing equipment that can simultaneously measure and report air pollutants at the refinery's fenceline.

Three types of open path systems are used, which measure along a 1 km light path and also evaluate meteorological conditions at the site. The remote sensing systems chosen were Fourier Transform Infrared (FTIR) Spectroscopy, Ultra Violet (UV) spectroscopy and Tuneable Diode Laser (TDL) Spectroscopy which measure 30 pollutant species, delivering data at 5 minute intervals continuously. Nine of the 30 chemicals measured are reported on a website (<http://www.cchealth.org/groups/hazmat/fenceline/>).

Summary

Fenceline monitoring is more complicated than just putting an instrument next to a fence or a boundary. Each site is different and has different requirements. Installations must be designed with care to obtain useful information and not to just

generate numbers. It is important that along with measuring pollutants, complementary meteorological data are logged simultaneously. With increasing environmental legislation and an onus on caring for the environment, sound, comprehensive, fenceline monitoring will be needed in the future.

Web links:

Integrated Pollution Prevention and Control (IPPC)
<http://www.defra.gov.uk/ENVIRONM/ENT/ppc/ippc.htm>

Sira Ltd./ROSE (Remote Optical Sensor Evaluation) EU Contract G6RD-CT2000-00434, see:
http://ec.europa.eu/research/growth/pdf/measuring-and-testing_4-060902-out_ec.pdf

Dr KIM HAMPTON
Lidar Technologies Ltd.

BIOGRAPHICAL NOTE: Kim Hampton is a systems advisor for Lidar Technologies Ltd (www.lidars.co.uk). She has a strong background in gas sensors and sensing for industrial and environmental applications. In her present role at Lidar Technologies, Kim divides her time between promoting Lidar (Light Detection and Ranging) techniques and assessing new applications for commercial Lidar systems. Kim Hampton gained a BSc and PhD in chemistry at the University of Leeds in Atmospheric Chemistry and then went on to work at the Max-Planck Institute for Chemistry, Mainz, Germany and the University of Bristol. Prior to her present appointment, Kim worked for Sira Ltd. as a senior research scientist, specialising in gas sensors and sensing. Kim is a committee member of the ECG.

Meeting report

Converting carbon dioxide into chemicals

Sequestering carbon dioxide captured from power plants is a viable technology for reducing the carbon emissions from fossil fuel combustion. However, are we missing an opportunity to exploit the captured carbon dioxide as a chemical feedstock?

This was the question posed to participants at a Royal Society of Chemistry workshop held at Burlington House on July 27th 2006. In this interactive workshop 50 participants had the opportunity to explore the chemical science behind the conversion of carbon dioxide into chemicals; to determine where the UK is in terms of academic expertise in the field and finally to indicate research priorities for the UK.

Summary of key points

Carbon dioxide can be converted into chemicals, fuels and polymers and there are technologies available today to achieve this. In context, the entire output of the chemicals industry (excluding fuels) is equivalent on a carbon basis to around 1-2% of the total annual anthropogenic carbon emissions

(6Gt). Therefore, chemicals based on CO₂ could contribute to reducing carbon emissions but not at a significant level; the synthesis of fuels (for example via Fischer-Tropsch chemistry) could substantially increase carbon emission reduction. CO₂ as a building block in long-lived polymers can be viewed as a mechanism to sequester carbon in the long-term. There are a number of potential technologies that require further research and development; for example the photochemical conversion of CO₂.

In the medium-term it is expected that fossil fuel power plants fitted with carbon capture and storage technologies will provide a source of relatively pure CO₂. In order to take advantage of this it is suggested that CO₂-to-chemicals technologies should be applicable at relatively low CO₂ pressures to avoid energy intensive pressurisation steps. It is important that CO₂ conversion technologies are developed alongside work on carbon capture and storage (CCS) technologies so that they can be considered in the design of pilot and full scale CCS plants.

The full life cycle analysis of technologies for converting CO₂ into chemicals must be considered. This will enable an unbiased assessment of the technology options as well as an

opportunity to compare against other carbon abatement technologies. It is also critical that an economic argument can be made to support technologies to convert CO₂ to chemicals.

Government and funding bodies should consider establishing a UK research centre with a focus on CO₂ chemistry. It is unclear whether this might be included in the remit of the recently announced energy and environmental research institute. In addition, to reduce the time for technological breakthroughs, funding mechanisms that allow researchers from outside of the EU to collaborate with UK research groups should be introduced. There is a need to attract, train, enthuse and retain high calibre talented young people in disciplines relevant to this field.

Web link to downloadable pdf files of all the presentations and a final report from this meeting:
<http://www.rsc.org/ScienceAndTechnology/Events/ConvertingCO2toChemicals.asp>

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Meeting report

The Investigation of Air Pollution Standing Conference

The Investigation of Air Pollution Standing Conference (IAPSC) was held at the NEC, Birmingham on Tuesday 5th December, 2006. More than 150 delegates attended, mostly from local authorities, but also representatives from Defra, the Environment Agency, monitoring and equipment consultants, academia and industry.

The subject of the morning session was *particulate matter* and was introduced by Richard Maggs (Bureau Veritas) with an overview of the 'UK Equivalence Programme for Monitoring of Particulate Matter', published by Defra in June 2006. The research compared a range of particulate monitors measuring PM₁₀ and PM_{2.5} at four locations representative of suburban, urban background, roadside and rural sites. Four of the monitors passed the equivalence testing without adjustment: Partisol 2025, FDMS (Filter Dynamics Measurement System) (PM₁₀ and PM_{2.5}) and Beta SM 200; whilst the TEOM (Tapered Element Oscillating Microbalance), the principal monitor employed by the national AURN (Automatic Urban Rural Network), failed. Defra intend to retrofit the existing AURN TEOMs with FDMS units commencing January 2007. However, local authorities are advised that their own TEOMs may still be used with the 1.3 correction factor until they become due for replacement.

Dave Green (KCL) followed with his 'Practical and Technical Experience of using the FDMS Unit' at eight sites in London. The FDMS removes the need for the 1.3 correction factor applied to TEOM measurements by introducing a 'purge' filter to the process. Comparison studies of TEOM 1.3, FDMS and gravimetric monitors showed comparable background concentrations. However, at roadside sites the FDMS unit recorded lower concentrations and up to four times fewer exceedences (e.g. Marylebone Road).

The difference in concentration between the FDMS and TEOM is

equivalent to the 'purge' filter measurement (i.e. TEOM 1.3 = FDMS Base + FDMS Purge) providing a more accurate correction factor than that recommended within the UK Equivalency trial report. Practical limitations of the FDMS unit were identified including potential leakages and the coarse temporal resolution of the data (hourly) which could mask operator error.

Gary Fuller (KCL) reported on 'Particulate Matter Relating to Waste Transfer Stations' at sites in London and south-east England, particularly within the immediate vicinity of residential properties. The contribution from waste transfer vehicles entering and leaving the site was observed as the main source, which may be attributable to resuspension of dust from the roads (observable from satellite imaging (Google Earth)) and/or suspension of dust from the vehicles themselves.

Toxicological analysis of the particulate matter revealed similar chemical components to building site waste, but with a greater hazard level. Road-sweeping has proven to be ineffective at reducing airborne particulate matter and the recommendation is to reduce the deposition of dust on to the roadway. It is estimated that in some cases reductions of 90% would be required to reduce particulate matter below National Air Quality Strategy (NAQS) guidelines. The EA, as regulators, are aware of the situation but enforcement is difficult.

The focus then moved to Europe where Wolfgang Thiel (Referat für Information und Marketing im Grazier Umweltamt)

(<http://www.feinstaubfrei.at>) described 'PM₁₀ Reduction Measures in Graz, Austria'. Situated within a basin in the Austrian Alps and prone to winter inversion events, Graz suffers extreme particulate matter episodes that have a



PM - CORRECT

A report recently issued by DEFRA announced that the TEOM-FDMS particulate monitoring system meets the equivalence requirements as defined in the relevant EC legislation. The TEOM-FDMS is the only system deemed equivalent for both PM₁₀ and PM_{2.5} without the use of a "correction" factor. Most existing TEOM users can update to FDMS at reasonable cost and benefit from the additional information on PM volatility and of course the 'correct' result without any "fiddle" factors.

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significant health impact. Transport and heating are the main sources of airborne particulates and measures to raise awareness and reduce the contribution from cars have been implemented, including ‘car free’ days and subsidising the retrofitting of filters to diesel vehicles. Despite these efforts, however, it is unlikely that Graz will meet EU guidelines and authorities are currently awaiting the new Euro5 Directive on emissions and exhausts.

Mike Woodfield (AEA Technology) concluded the morning session with his commentary on ‘Sources of PM_{2.5} in Europe’ as detailed in the updated ‘EMEP/CORINAIR Emission Inventory Guidebook – 2005’ (<http://tfeip-secretariat.org/unece.htm>). It was observed that domestic combustion and municipal waste appear to contribute a greater percentage to PM_{2.5} than PM₁₀ but the contribution from agriculture is less.

The afternoon session focussed on *social equity and air quality*, commencing with a social history of air

pollution ‘50 years on from the Clean Air Act’ from Peter Brimblecombe (UEA). The presentation concluded that although London no longer suffers the dense smogs of the 1950s – thanks in part to the measures introduced by the Clean Air Act 1956, but also due to changes in industry and social practices – the ‘Big Smoke’s’ current health problems are now associated with traffic pollution.

This was followed by Ioanna Gegisian’s (UWE) presentation of her PhD research examining ‘Environmental Justice: What does it mean for LAQM?’ This EA-funded project is looking specifically at Air Quality Management Areas (AQMA) and deprivation indices, examining how social deprivation is addressed in Air Quality Action Plans (AQAPs). Through surveys, questionnaires and interviews with local authorities, Ioanna observed that social and wider economic impacts were the two least considered objectives in the selection process used to create Action Plans and that integration of AQAPs with other

documents was hampered by a lack of communication between departments and incompatible deadlines.

Steve Moorcroft (Air Quality Consultants) spoke about the ‘Exposure Reduction Approach and Implications for Social Equity’. The Café Directive proposed exposure reduction targets for PM_{2.5} of 20 – 25 µg m⁻³ (target value 2010/ limit value 2015). The advantage of the Exposure Reduction approach, given that there are no “safe” levels of particulate matter, is that it does not imply a threshold. Exposure-reduction uses a percentage rather than limit values to maximise health benefits and social equity by driving down pollution levels continuously. Reducing the focus on limit values should also reduce the role of local authorities.

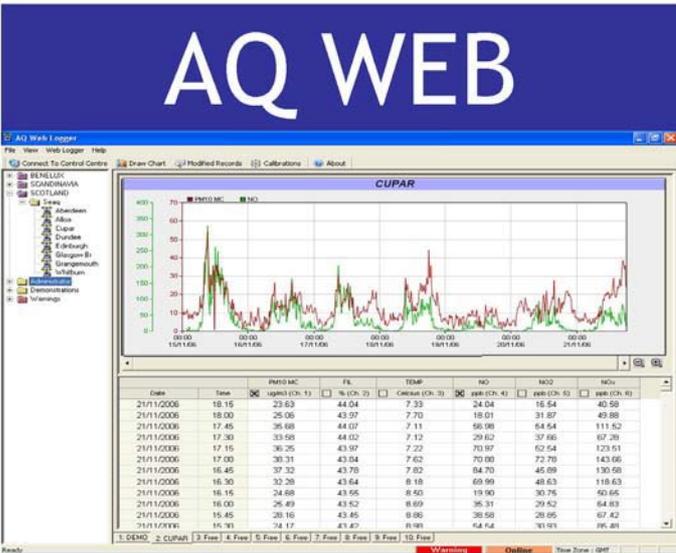
Steve observed that traffic pollution problems are often caused by people outside of the affected communities, who can afford to avoid the effects of their actions. In addition people in deprived areas are less likely to have cars and are therefore less likely to be contributing to the problem themselves. It was also suggested that measures to reduce background PM_{2.5} are ineffective and that it is therefore better to target hotspots. Funding for mitigating measures may be sought from developers under PPS 23 Appendix 1G. It was also noted that further to the AURN upgrades mentioned in Maggs’ presentation earlier, approximately 70 more PM_{2.5} monitoring stations will be required to supplement the national monitoring network.

The concluding presentation was given jointly by Steve Simmons and Rebecca Brown representing the five local authorities bidding for the current round of Beacon status (Croydon, Greenwich, Kensington and Chelsea, Sefton and Sheffield). This year air quality is a core feature of the Beacon status award, and these Councils have initiated a number of measures designed to reduce air pollution in their areas.

Web link: Investigation of Air Pollution Standing Conference
<http://www.iapsc.org.uk/papers.html>

JO BARNES
 Air Quality Unit,
 Cornwall College,
 December 2006

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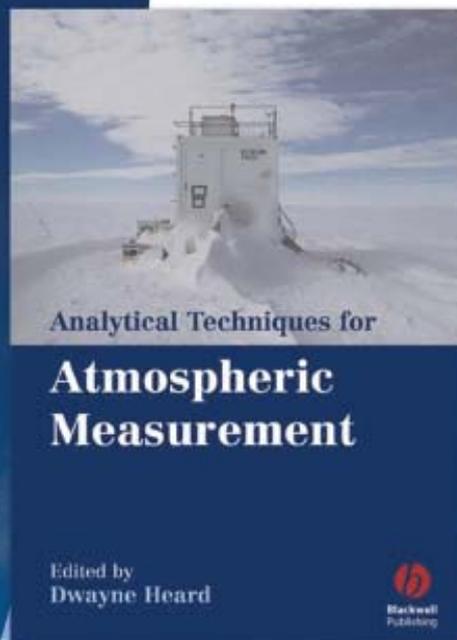
Analytical Techniques for Atmospheric Measurement

Edited by Dwayne Heard

*Professor of Atmospheric Chemistry
at the University of Leeds, UK.*

Written as an authoritative guide to the techniques of instrumental measurement for the atmospheric scientist, research student or undergraduate, *Analytical Techniques for Atmospheric Measurement* focuses on the instruments used to make real time measurements of atmospheric gas and aerosol composition.

Topics covered include how they work, their strengths and weaknesses for a particular task, the platforms on which they have been deployed and how they are calibrated. It explains the fundamental principles upon which the instrumental techniques are based (ie what property of a molecule can be exploited to enable its detection), what limits instrumental sensitivity and accuracy, and the information that can be gained from their use.



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£99.50 | Hardback | Publishing 2007

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Renewable Energy

This reference work covers the subject at the scientific and political level. Chapters have general introductory sections, followed by more advanced topics.

NETLIBRARY

Chemical Consequences: Environmental Mutagens, Scientist Activism, and the Rise of Genetic Toxicology

An historical and sociological account of the development of genetic

toxicology. Includes a list of the top ten journals for information on chemical mutagenesis.

Environmental Laboratory Exercises for Instrumental Analysis and Environmental Chemistry

Presents detailed tested experiments along with background information, safety and hazard notes, and data collection sheets.

Nanotechnology: Environmental Implications and Solutions

Discusses the control, reduction and elimination of the environmental and related problems associated with nanotechnology.

KNOVEL

Handbook of Environmental Degradation of Materials

Outlines the costs of material degradation, and explains how to measure, analyse, and prevent environmental degradation for a wide range of industrial materials. Provides case studies of how to cope with the degradation of metals and polymers under adverse environmental conditions.

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Enquiries may be sent to <http://www.rsc.org/Library/Forms/EnquiriesRequestForm.asp> or library@rsc.org

If you have any further questions please email Nazma Masud at library@rsc.org

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Recent books on the environment and on toxicology at the RSC library

The following books and monographs on environmental topics, toxicology, and health and safety have been acquired by the Royal Society of Chemistry library, Burlington House, during the period July to December 2006.

An Introduction to Pollution Science

R. M. Harrison (ed.),
Royal Society of Chemistry,
Cambridge, 2006,
ISBN/ISSN: 9780854048298,
Accession No: 20060209,
628.52

Cobalt and Inorganic Cobalt Compounds

(IPCS Concise International Chemical Assessment Document No. 69)

J. H. Kim; H. J. Gibb; P. D. Howe,
World Health Organization, Geneva
2005,
ISBN/ISSN: 9789241530699,
Accession No: 20060230,
628.5

Contribution to the Methodology for the Development of Acute Exposure Threshold Levels in Case of Accidental Chemical Release
(ECETOC Technical Report No. 100)

M. Gribble (ed.),
European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels
2006,
ISBN/ISSN: 07738072100,
Accession No: 20060226,
615.9

Introduction to Toxicology, 2nd edition

J. A. Timbrell,
Taylor & Francis, London 1995,
ISBN/ISSN: 0748402411,
Accession No: 20060195
615.9

Photodynamic Therapy with ALA: A Clinical Handbook

(Comprehensive Series in Photochemical & Photobiological Sciences: Vol. 7)

R. Pottier; B. Kramer; H. Stepp; R. Baumgartner, R. (eds.),
Royal Society of Chemistry,
Cambridge, 2006,
ISBN/ISSN: 9780854043415,
Accession No: 20060250,
615.831

'Surely That's Banned': A Report for the Royal Society of Chemistry on

Chemicals and Procedures Thought to be Banned from Use in Schools

Royal Society of Chemistry,
Cambridge, 2006,
Accession No: 20060248,
614.8

Synthetic Amorphous Silica (CAS No. 7631-86-9)

(ECETOC Joint Assessment of Commodity Chemicals No. 51)

M. Gribble (ed.),
European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels,
2006,
ISBN/ISSN: 0773-6339-51,
Accession No: 20060259,
615.9

Toxicological Modes of Action: Relevance for Human Risk Assessment

(ECETOC Technical Report No. 99)

M. Gribble (ed.),
European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels,
2006,
ISBN/ISSN: 0773807299,
Accession No: 20060227,
615.9

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The science of climate change: A Royal Society showcase of the IPCC 4th Assessment Working Group 1 Report

Thursday 1st to Friday 2nd March 2007

Venue: **The Royal Society**, 6-9 Carlton House Terrace, London SW1Y 5AG

Organised by Professor Peter Cox, Professor Brian Hoskins CBE FRS, Professor John Mitchell OBE

FRS, Dr Tim Palmer FRS and Professor John Pyle FRS.

Climate change is one of the most important challenges of our time. In 2001 the Intergovernmental Panel on Climate Change (IPCC) highlighted that human activities are causing concentrations of greenhouse gases to rise at a rate that is unprecedented in the last 20,000 years and carbon dioxide levels are now higher than they have been for 650,000 years. Since 2001 our understanding of the world's climate system and the role of human activity has increased.

This meeting will showcase "The science of climate change" working

group 1 report. The event will highlight the main findings of the report, particularly those areas likely to be of specific interest to the scientific and policy community. The emphasis will be on the advances in our understanding of the science and causes of climate change, since the Third Assessment Report in 2001, and identifying new research priorities and knowledge gaps.

Register for this event

Event Programme -
<http://www.royalsoc.ac.uk/trackdoc.asp?id=3494&pId=5464> (Adobe PDF File)

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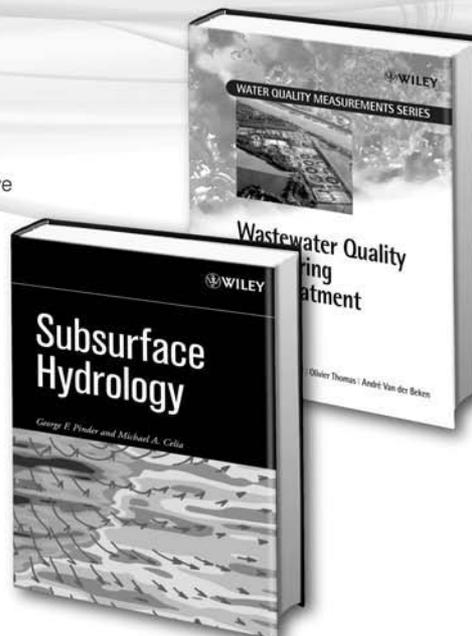
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