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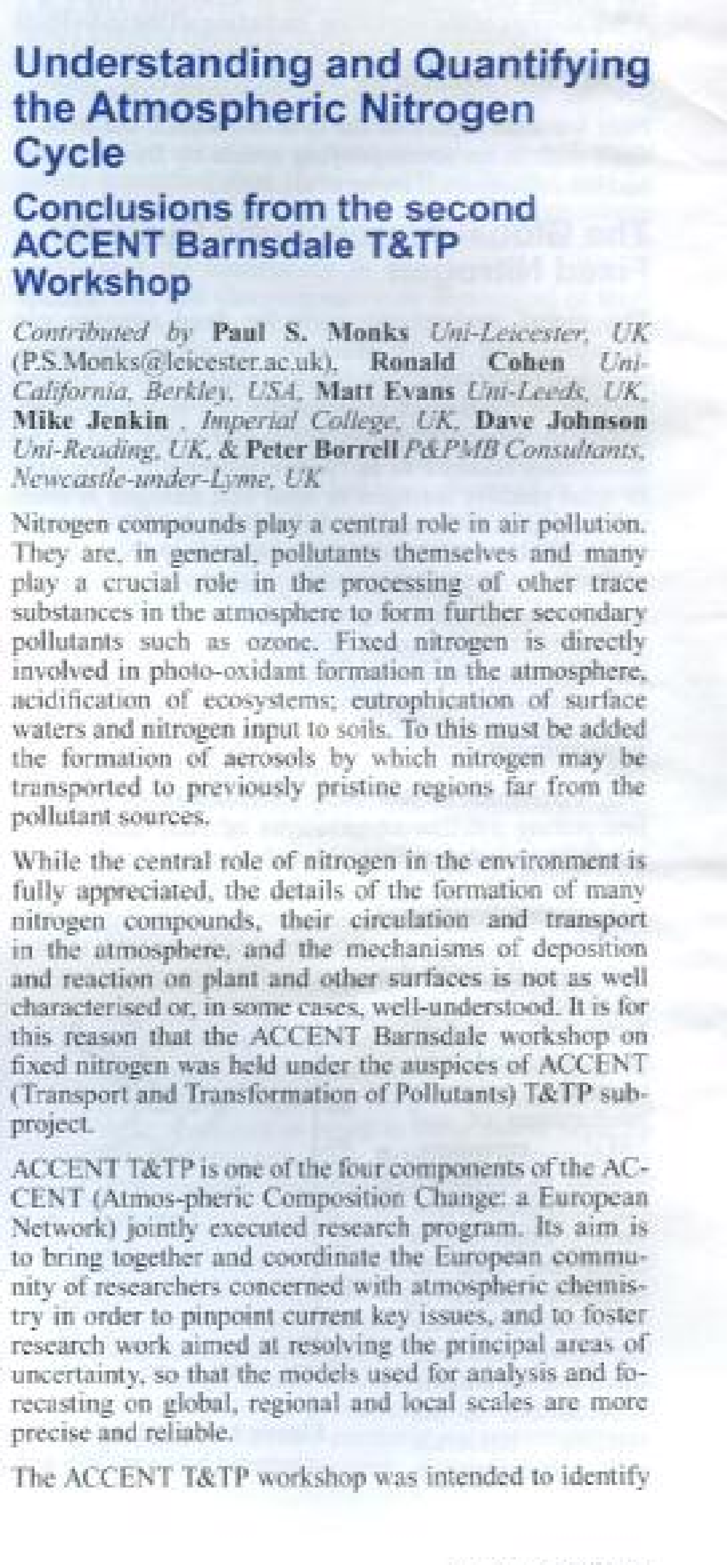

Understanding and Quantifying the Atmospheric Nitrogen Cycle

Conclusions from the second ACCENT Barnsdale T&TP Workshop

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Nitrogen compounds play a central role in air pollution. They are, in general, pollutants themselves and many play a crucial role in the processing of other trace substances in the atmosphere to form further secondary pollutants such as ozone. Fixed nitrogen is directly involved in photo-oxidant formation in the atmosphere, acidification of ecosystems; eutrophication of surface waters and nitrogen input to soils. To this must be added the formation of aerosols by which nitrogen may be transported to previously pristine regions far from the pollutant sources.

While the central role of nitrogen in the environment is fully appreciated, the details of the formation of many nitrogen compounds, their circulation and transport in the atmosphere, and the mechanisms of deposition and reaction on plant and other surfaces is not as well characterised or, in some cases, well-understood. It is for this reason that the ACCENT Barnsdale workshop on fixed nitrogen was held under the auspices of ACCENT (Transport and Transformation of Pollutants) T&TP subproject.

ACCENT T&TP is one of the four components of the ACCENT (Atmos-pheric Composition Change: a European Network) jointly executed research program. Its aim is to bring together and coordinate the European community of researchers concerned with atmospheric chemistry in order to pinpoint current key issues, and to foster research work aimed at resolving the principal areas of uncertainty, so that the models used for analysis and forecasting on global, regional and local scales are more precise and reliable.

The ACCENT T&TP workshop was intended to identify and review the key uncertainties in the land-atmosphere, atmospheric and laboratory data for nitrogen cycling and to provide a basis for future collaborative research priorities in this area. There were three topic areas addressed:

1. The global atmospheric cycle for fixed nitrogen.
2. Uncertainties in the atmos-pheric chemical processing of nitrogen compounds.
3. Surface – atmosphere exchange of fixed nitrogen.

A full account of the workshop, including all the individual contributions and the detailed references, is available in the ACCENT report of the workshop (Cox et al., 2006).

Here we shall report on the first two topics; the third is dealt with in an accompanying article by David Fowler and his colleagues (Fowler et al., 2006).

The Global Atmospheric Cycle for Fixed Nitrogen

The global atmospheric cycle for fixed nitrogen can be represented by the processes describing emissions, chemical transformations, transport and removal. Several reviews of the subject are available (e.g Galloway et al., 2004). By way of definition NO_x is $NO + NO_2$ and is also sometimes referred to as "active nitrogen". The sum of total reactive nitrogen or total odd nitrogen is often referred to as NO_y and can be defined as $NO_y = NO_x + NO_3 + 2N_2O_5 + HNO_3 + HNO_4 + HONO + PAN + MPAN$ + nitrate + alkyl nitrate. NO_y can also be thought of as NO_x plus all the compounds that are products of the atmospheric oxidation of NO_x. NO_z is NO_y-NO_x. The meeting was comprised of highlights of recent progress and a discussion of open questions.

Emissions

NO_x emissions in low NO_x environments. Research interpreting satellite observations of NO_2 shows it is possible to translate observations of column concentrations into emissions and thus provide global information on NO_x sources. For example, Jaegle et al. (2005) suggest that soil emissions may be underestimated by a factor of two. Bertram et al. (2005) show that satellite data can go beyond a simple scaling factor of a priori emissions and can be used to constrain mechanisms of soil NO_x emissions. Richter et al. (2005; Figure 1) showed how these observations could be used to diagnose trends in NO_x emissions over the globe. However, there are significant uncertainties in the satellite retrievals and interpretation which still have to be resolved. The discussion em that these and other results are just beginning to the incredible potential of the satellite data sets.

Processing

NO_x sinks. The hydrolysis of N_2O_5 on aeros significant sink for NO_x, converting it into H models, approximately 30% of all HNO_3 pr occurs through N_2O_5 hydrolysis, with N accounting for 40% and the remainder i reactions of organic species and NO_x (Liao and 2005). Uptake coefficients for the hydrolysis aerosols were originally derived for the stratosp used cold sulfuric acid as the aerosol. In the trop aerosol composition is different and both temp and relative humidities are higher. Recently, la studies have been undertaken for a better descripti rate of hydrolysis of N_2O_5 within the troposphere workshop, Matt Evans described how these impro have had a significant impact on the global concen of NO_x, O_3 and OH, increasing them globally v model by 7 %, 4 % and 8 % respectively.

Contributions from Paul Griffiths showed that u N_2O_5 onto mixed phase aerosols containing both and inorganic components was slowed by the pres the organics. This phenomenon has not been con in global models. Recent advances in obser capability for NO_3 and N_2O_5 have allowed the of N_2O_5 hydrolysis to be tested directly in the fi Brown et al. (2006) show values of γ (uptake coef varying by orders of magnitude on ambient aeroso

Role of NO_3 as an oxidant. NO_3 can act as a oxidant during the night time, initiating the ox of VOCs. Recent evidence described by Stuart P and Steve Ball from aircraft-borne NO_3 instrume and remote DOAS and LIDAR techniques and has a 'cloud' of elevated NO_3 at the top of the conti boundary layer which was unobservable with pr techniques. The existence of such NO_3 'clouds have a significant impact on the processing of pol within the boundary layer and on their export to th atmosphere.

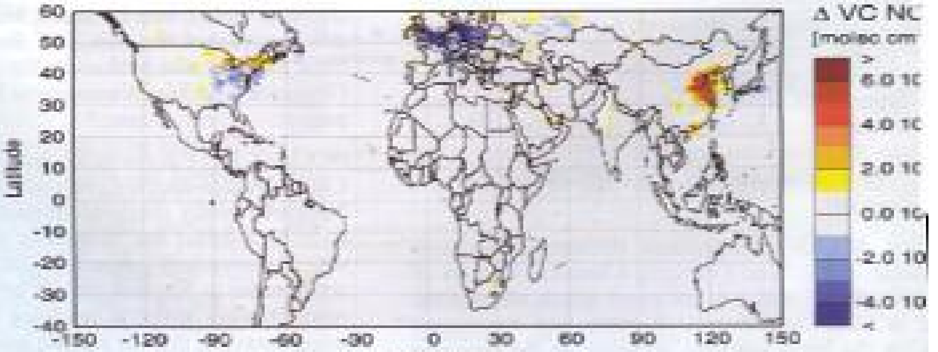

Figure 1. Annual changes in the tropospheric NO_2 column as derived from GOME measurements between 1996 and 2002. *Courtesy of Andreas Richter* (Richter *et al.*, 2005).

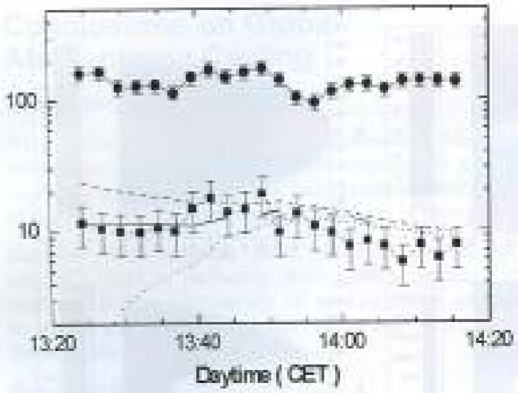

Figure 2. Comparison of measured HONO concentrations with model predictions for a pure gas phase mechanism: —●— denotes the measured HONO data; —■— denotes the photostationary state (PSS) calculation; the different lines represent time-dependent model runs with different starting values: [HONO]initial = 0(……), [HONO]initial = [HONO]PSS (——), and [HONO]initial = 2×[HONO]PSS (--------). Error bars on the PSS values denote the accuracy due to experimental uncertainties of the input parameters. *Courtesy of Andreas Hofzumahaus* (Cox et al. 2006).

Production of HONO. Andreas Hofzumahaus described fluxes of HONO through a forest which were extremely high and difficult to reconcile with current understanding, as it suggests a photo-enhanced heterogeneous source (Figure 2). This source had significant impacts on the HO_x and NO_x badgets within the forest. It is thought that this might involve complex uptake and processing of NO_x on water surfaces within the forested environment.

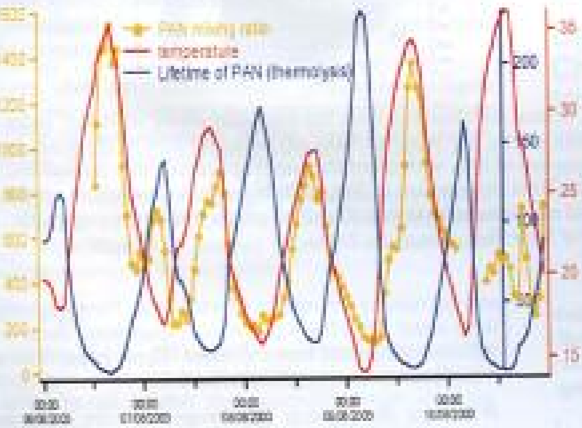

Figure 3. PAN, isoprene mixing ratios and air temperature, and the calculated instantaneous lifetime of PAN over the heatwave period (6th – 10th August, 2003) in the UK (Lee *et al*., 2006).

Other observations of HONO -- notably from the Polar Regions -- also appear inconsistent with our current understanding of HONO photochemistry (e.g. Beine et al., 2002).

Organic Chemistry. Matt Evans described how observations of high CH_3CHO concentrations in remote areas appear to be inconsistent with observations of PAN and our current understanding of the photochemistry associated with these species. This discrepancy may reflect the difficulties of making observations of CH_3CHO. However, if the observations are correct this poses a severe challenge to our understanding of NO_x and NO_y processing within the atmosphere. The oxidation of complex hydrocarbons (notably isoprene in NO_x rich regions) leads to the production of PANs and other nitrates. The chemistry of these species is complex and poorly quantified. Ron Cohen and Paul Monks (see for example Figure 3) described the impact of this chemistry on the composition of the boundary layer. Mike Jenkin highlighted the uncertainty in the chemistry of these species. The fate (decomposition or deposition) of these species can have a significant impact on the composition of the atmosphere.

Halogen chemistry. Observations of reactive halogen species (notably BrO and IO) would suggest a sink of NO_x through the hydrolysis of $BrNO_3$ and INO_3 on aerosol surfaces. This sink has been observed in Arctic ozone depletion events. However, quantifying the global significance of this sink is not currently possible owing to a lack of observations of halogen species outside of the boundary layer.

Response of the biosphere to changing emissions. The biosphere will respond to changes in N emissions in a variety of ways and through a variety of mechanisms. For example increased global emissions of N may increase N deposition, enhancing biosphere growth; however it may lead to higher O_3 concentrations which may lead to plant damage inhibiting growth. It is unclear how the biosphere has and will respond to changing nitrogen emissions.

Transport

Convection. Convection is important for determining the global distribution of many species. It causes the vertical redistribution of species, wet deposition of species and the production of lightning NO_x. Global models treat these processes as being to some extent separate and unconnected. Thus, they have a poor ability to accurately represent the extent of vertical transport.

Subgrid issues. A wide range of sub-grid issues exist in determining the composition of the atmosphere. The non-linear nature of the chemistry, in-homogeneity of emissions and depositions, scales of atmospheric motion, etc., all lead to errors in models due to the assumed grid scale. There is currently no systematic way of addressing these issues. Steve Ball described the impact of small-scale variability on chemical composition, highlighting the impact of isoprene emissions on the small scale distribution of O_3 and NO_3 (see Figure 4).

Boundary layer issues. Our understanding of the movement of material within the boundary layer under stable, low diffusivity situations appears weak with impacts on the surface concentration of species and their distribution through the atmosphere.

Sinks

Ammonia. Ammonia sinks and sources are complicated, highly coupled and variable on very small scales. Thus, the concept of separate ammonia emission inventories and deposition mechanisms are inappropriate.

Organic nitrogen species. The processes by which organic nitrogen species are lost through wet and dry deposition are badly quantified and highly uncertain. The wet deposition of PAN to fogs appears to occur but it is not understood how this occurs. Whether isoprene nitrates are deposited is uncertain but is significant for NO_y, NO_x and O_3 distributions over isoprene rich regions. Uncertainty over these depositional sinks of organic NO_y lead to uncertainty over the global distribution of NO_x and NO_y.

Deposition within models. Deposition schemes within global models are old and do not include recent advances. Stevenson highlighted the substantial difference between models in their attribution of NO_y deposition to wet or dry mechanisms. Uncertainties remain over which processes limit the dry uptake of HNO_3, and the appropriate treatment of the deposition of aerosols.

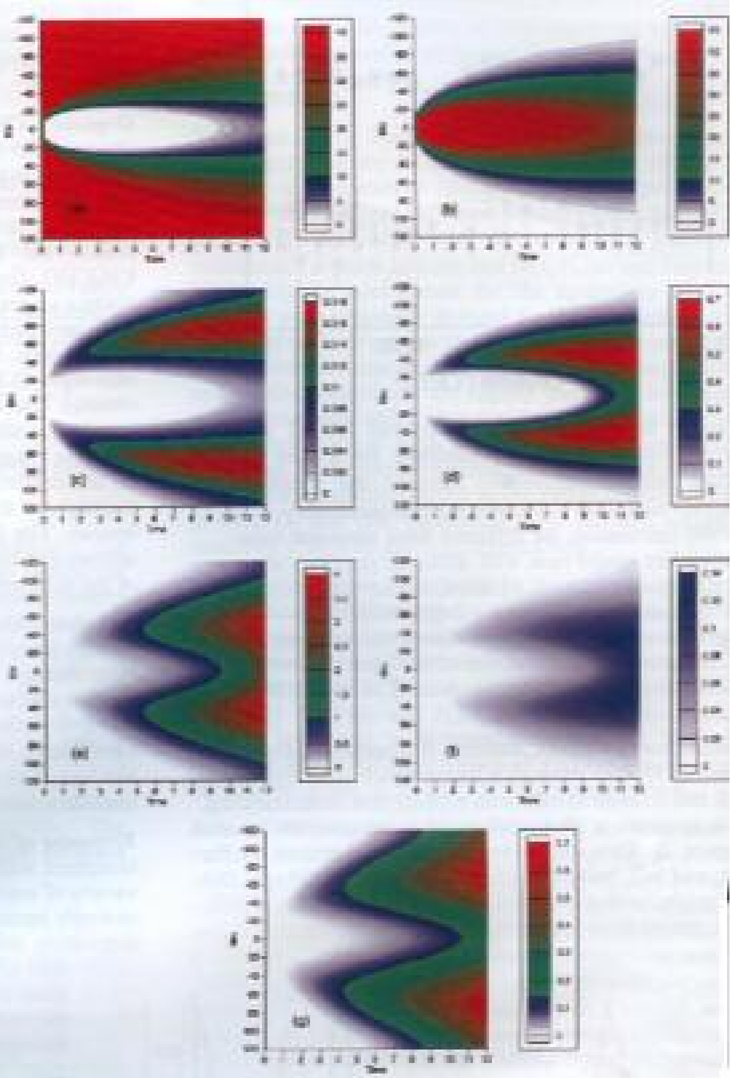

Figure 4. Spatial distributions from the Gaussian plume model of Jones *et al.* (2005): (a) O_3, (b) NO_2, (c) NO_3, (d) N_2O_5, (e) HNO_3, (f) products from the reaction of NO_3 with co-emitted anthropogenic hydrocarbons and (g) products from the reaction of NO_3 with biogenic hydrocarbons in the background atmosphere. Note that (f) and (g) are plotted on the same scale (*Courtesy of Steve Ball; Cox et al., 2006*)

Impacts

Anthropogenic nitrogen in the biosphere. The response of the biosphere to increased nitrogen levels is complex. Understanding the full response will require complex coupled models. The answer also depends upon the timescale, the region being investigated and the nature of the problem.

Impact on SOA. Mike Jenkin discussed the impact of nitrogen upon Secondary Organic Aerosol composition and Gordon McFiggins discussed the role of nitrogen upon inorganic and organic aerosols. Both of these influence the ability of aerosol to act as cloud condensation nuclei and the subsequent uptake of water onto these aeros form cloud. This has a potential impact upon the ae indirect effects and hence climate. These impacts ar considered in current climate models.

What are the impacts of nitrogen species on hu health? Lise Frohn discussed work quantifyin impact of nitrate aerosol on human health through th of linked atmospheric-health models and highlig potential of links for the health community.

Conclusions on Global Atmospheric Cycling

Emissions

NO_x emissions in low NO_x environments. More observations of nitrogen species are required in a wider variety of environments to test our current understanding of the processes controlling the emissions of nitrogen.

Satellite observations. More observations of NO_2 and NO_y, and in particular their vertical profiles, are required in a wider variety of environments in order to assess satellite retrieval algorithms and to aid in the interpretation of satellite data.

Processing

NO_3 sinks. There remain significant uncertainties in the rates of reactive uptake of N_2O_5 onto aerosols. Further laboratory studies of uptake onto different aerosol types under different temperature and relative humidity regimes are needed to reduce this uncertainty. Field observations of N_2O_5 and NO_3 concentrations are needed to test model predictions.

Role of NO_3 as an oxidant. More observations are needed of the distribution of NO_3 over a variety of regions and timescales to assess the extent of the impact of NO_3 chemistry and its vertical distribution.

Production of HONO. Increased observation datasets of HONO within a variety of environments and conditions are needed, as are laboratory studies of the potential heterogeneous production mechanisms for HONO.

Organic chemistry - 1. An assessment of the quality of CH_3CHO observations should be made to validate the observations made in remote regions.

Organic chemistry - 2. The chemistry of the complex organics species produced by the oxidation of isoprene in the presence of NO_x should be studied in more detail both in the laboratory and in the field.

Halogen chemistry. Observations of reactive halogen species over a variety of environments and conditions would allow an evaluation of the impact of halogen chemistry on NO_x concentrations.

Response of biosphere to changing emissions of oxidized and reduced nitrogen. Coupled biosphere-chemistry-climate simulations are needed to assess the impact of changing emissions on the planet.

Transport

Convection. Links between the meteorologists and the atmospheric composition modelling community should be strengthened so that the parameterization of these processes can be done on the best possible footing.

Subgrid issues. Approaches to investigating sub-grid scale issues should be developed, evaluated and considered for implementation into global models of the atmospheric cycling of N.

Boundary layer issues. We should improve our understanding of the transport of species through the boundary layer under stable conditions through field and computer experiments.

Sinks

Ammonia. The emission and deposition of ammonia should be considered as a single process with appropriate parameterization within models.

Loss of organic nitrogen species. More detailed process studies of the removal of organic NO_y from the atmosphere are needed to quantify this issue.

Representation of deposition within models. Recent advances in our knowledge of the fundamental processes leading to the deposition of nitrogen species should be included in models. Mechanisms to represent the sub-grid nature of deposition should also be developed and implemented.

Impacts

The impact of anthropogenic N on the biosphere. Coupled biosphere and atmosphere models are needed to fully understand the impact of anthropogenically emitted nitrogen on the atmosphere. They need to contain a full representation of the chemical and biological systems that process nitrogen.

The impact of nitrogen species on the climate properties of aerosols. The impact of inorganic and organic nitrogen species on cloud properties should be investigated and suitable parameterizations developed for climate models.

The impacts of nitrogen species on human health. The links between the global observational and modelling community and the health impact communities should be strengthened so that each can benefit from the experience of the other. (See accompanying article by Frank Raes).

Uncertainties in the Atmospheric Chemical Processing of Fixed Nitrogen

The principal questions addressed were as follows.

- What new measurements (either in the laboratory or in the field) are needed to test or confirm our understanding of the chemical changes occurring during the atmospheric processing of oxidised forms of nitrogen?
- Which are the key areas where improved chemical parameters and mechanisms are required for our quantitative understanding of the atmospheric processing of nitrogen?
- What are the main limitations in representing the current knowledge of the atmospheric processing of oxidised nitrogen species in atmospheric models?

New measurements required. Much of the discussion of what new measurements are required was related to the problem of understanding the complex chemistry

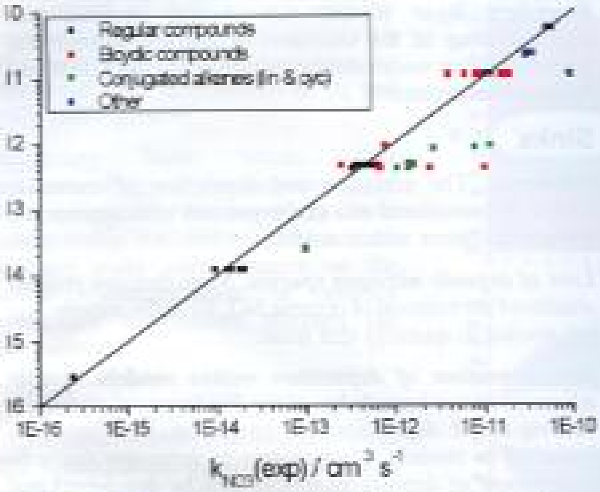

Figure 5. Comparison between the experimental rate coefficients for NO_3+alkene reactions and rate coefficients predicted using the SAR. "Other" indicates nearly-conjugated alkadienes, where the two double bonds are separated only by a single —CH_2— group. *Courtesy of Luc Vereecken* (Cox *et al.*, 2006).

occurring not only in the gas-phase but also on surfaces. Implicit with a discussion of desired new measurements is the identification of key areas where an enhanced understanding of the chemical processes involved in the atmospheric transformation of oxidised nitrogen-containing species would lead to the greatest improvements in our quantitative understanding of the atmospheric nitrogen cycle. Specific examples will be expanded upon in the next section.

In terms of gas-phase chemistry, the detailed kinetics of the reaction of OH with NO_2, to form HNO_3, are still relatively uncertain (ca. ±30 %) (Atkinson et al., 2004) and under polluted urban conditions may in fact be the major source of uncertainty in quantitatively understanding the fate of atmospheric nitrogen. In comparison to this well-studied "daytime" sink for atmospheric nitrogen (obviously, HNO_3 can readily be lost from the atmosphere) the nighttime formation of HNO_3 is much less certain – this uncertainty is essentially due to the hydrolysis of the N_2O_5 on aerosol surfaces (Evans and Jacob, 2005). Data were presented which showed that, in laboratory experiments, the efficiency of this process is significantly reduced when oligomeric hydrocarbon material is present in/on the aerosol – presumably with a surface excess. It is becoming increasingly clear that such large molecular weight organic material is intimately involved with the formation and growth of secondary organic aerosol (SOA) material. The kinetics and mechanisms of SOA formation are very uncertain and so, necessarily, are the effects of the formation of oligomeric oxidised hydrocarbon material on the efficiency of N_2O_5 hydrolysis processes. Also related to this area is the potential significant inclusion of (semi- and non-volatile) organic nitrogen-containing species into SOA. Whilst it is clear that the presence of oxynitro-substituents (-ONO_2) in organic species lowers

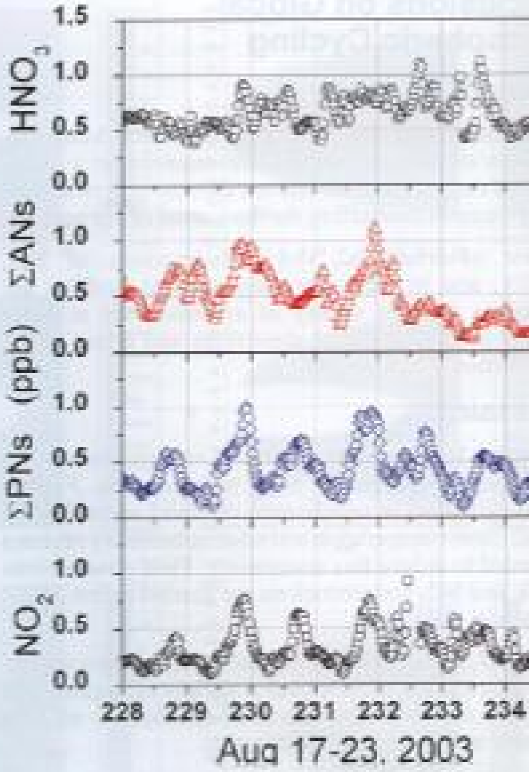

Figure 6a. Example field data for ambie measurements of NO_2, HNO_3, alkyl nitrates (A and peroxyacyl nitrates (AN) (Cox *et al.*, 2006).

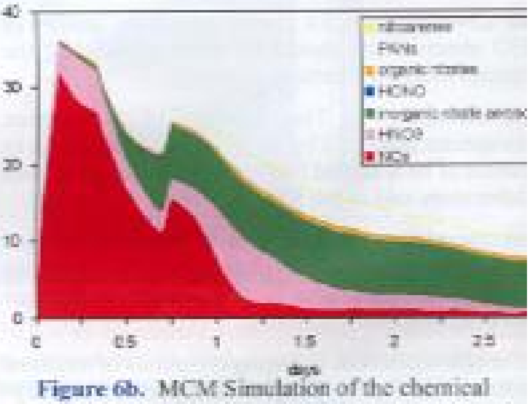

Figure 6b. MCM Simulation of the chemical cycling of oxidised forms of nitrogen as a functio of time for an idealised air trajectory. After two days processing, 30% of the components are organic in nature (Cox *et al.*, 2006).

their saturation vapour pressure (and hence increase propensity to transfer from the gas-phase to a cond organic-phase), very few such data are available can be used to formulate reliable estimation metho these physical properties.

In general, the atmospheric chemistry (formati degradation kinetics and mechanisms) of organi species are not well understood. For instance, ve formation yields of organic nitrate species ($RONO_2$) from the reactions of organic peroxyl radicals (RO_2) with NO, have been measured in the laboratory, yet for atmospheric chemistry it is important to understand how these yields vary with the structure of RO_2 and in parameter-space (temperature and pressure). Those reactions studied also need to be understood in terms of chemical theory in order to be able to reliably estimate $RONO_2$ formation efficiencies for radical intermediates (very many of which are atmospherically important) which have not and cannot be measured in the laboratory. There was a common theme in the discussion of uncertainties in the atmospheric chemical processing of nitrogen compounds that structure activity relationships (SARs) are ultimately needed in order to be able to predict rate parameters, and ideally product yields, for reactions which cannot be measured in the laboratory. Such SARs are founded on extensive, systematically varied and reliable databases of laboratory rate data. In addition to estimating unknown rate data, SARs can also help to point out where there may be details lacking in the understanding of reaction mechanisms. For example, where a SAR starts to break down – but where it works well for a range of model chemical species – this may be due to secondary effects beginning to govern the kinetics. These may include a change in mechanism – such as evidence for H-abstraction in the reactions of certain alkene species with NO_3 (Figure 5).

Where the understanding of the atmospheric degradation of organic NO_y species (e.g. the reactions of NO_3 with alkenes and the reactions of OH with $RONO_2$) would certainly benefit from more rate data, they would at least equally benefit from product studies.

During the plenary presentation for the global atmospheric cycle for fixed nitrogen (made by Ron Cohen) field data were presented which represented measurements of the concentration of HNO_3, the total concentration of alkyl nitrates ($\sum RONO_2$) and the total concentration of peroxyacyl nitrates ($\sum RO_2NO_2$) (Figure 6a). These measurements were made by thermally dissociating ambient air samples (over prescribed temperature ranges) and detecting the concentration of liberated NO_2 by laser induced fluorescence (LIF). Such measurements afford an unprecedented opportunity for comparing measured ambient organic NO_y data with the results of simulations using very detailed chemical mechanisms, for example the Master Chemical Mechanism (MCM) (Figure 6b).

Key Areas for Research

Areas where directed research would most benefit our quantitative understanding of the atmospheric chemical processing of nitrogen compounds concerned much of the material mentioned in the previous section in addition to others where a picture of the chemistry is just emerging. In terms of the established view of atmospheric nitrogen cycling, laboratory kinetic and mechanistic data concerning the atmospheric formation and processing of organic NO_y would be extremely beneficial, particularly in understanding the efficiency with which nitrogen is cycled between NO_x and NO_y forms. The links between semi-/non-volatile organic NO_y species and SOA need to be elucidated – for example, measurements revealing the significant presence or absence of multifunctional organic nitrate species in ambient fine aerosol material would be extremely illuminating.

In terms of emerging areas of research, the global atmospheric scope of surface-mediated, photosensitised formation of HONO from NO_2 needs to be established. In a more indirect, but by no means insignificant, sense the reactive involvement of NO_x in alkene ozonolysis reactions needs to be elucidated. For example, it is now well established that this class of reaction can be a major – and indeed sometimes dominant – source of HO_x (Heard et al., 2004) radicals but it is not at all known if the carbonyl oxide (Criegee) intermediates from which, for example, OH is formed can react with NO (Ariya et al 2000, Paulson and Orlando, 1996). Criegee intermediates are similar in structure to organic peroxyl radicals and hence are expected to react with NO (yielding NO_2 and a carbonyl). If these bimolecular reactions are sufficiently fast then, under given atmospheric conditions, they may effectively out-compete the decomposition of Criegee intermediates – i.e. these latter reactions may not be a significant direct source of HO_x radicals in the atmosphere. The NO_x-dependence of OH yields from ozone-alkene reactions need to be investigated (Calvert et al., 2000). The experimental complication associated with such studies – and the reason that none have been reported to date – is that ozone (O_3; i.e. one of the reactants) is reactive towards NO. Related to this area of chemistry is the NO_x-dependence of SOA yields from the ozonolysis of monoterpene species, for example α-pinene. Data presented by Neil Donahue (Donahue et al., 2005) at the Faraday Discussion meeting that showed the SOA yield (expressed on a mass basis) from the reaction of ozone with α-pinene decreases significantly in the presence of added NO. It is not clear whether this latter effect is due to reactions of α-pinene Criegee intermediates with NO (giving rise to more fragmentation and the production of more volatile reaction products in the degradation mechanism) or due to a perturbation of the complex peroxyl radical-peroxyl radical reactions which occur in the absence of NO in the majority laboratory experiments (i.e. NO converts peroxyl radicals to alkoxyl radicals).

Representing Nitrogen Processing in Atmospheric Models

The inclusion of the detailed processes described above in atmospheric models was discussed but a significant point is that the size of chemical modules within global models is not likely to increase significantly in the near future. This is due, in part, to the need to significantly increase/enhance other modules within models, such as those describing aerosol chemistry and physics. Again, on the theme of global modelling, although the overall aim is to represent complex chemistry efficiently, the chemistry of species such as isoprene needs to be represented more explicitly. Obviously, this requires a better experimental and theoretical understanding than we currently have of the atmospheric oxidation of this very important hydrocarbon and it's interactions with the atmospheric nitrogen cycle. In essence, to most reliably produce efficient, reduced chemical mechanisms it is necessary to start with very detailed, "trusted" mechanisms against which smaller mechanisms can be tested.

Conclusions on the Atmospheric Chemical Processing of Fixed Nitrogen

Much is already understood about the atmospheric processing of oxidised nitrogen species. However, understanding of the following chemical processes is particularly uncertain:

- The role of developing SOA material in changing the rate of N_2O_5 on aerosol surfaces
- The detailed chemistry of organic NO_y species – both their formation and degradation
- The significance of multifunctional organic nitrate species for the formation and growth of SOA material
- The atmospheric significance of HONO formation from surface-mediated, photosensitised reactions of NO_2
- The perturbation of direct HO_x formation and SOA formation from the ozonolysis of alkene-species

In order to reduce some of these uncertainties, proposed research activities include:

- Further laboratory studies of the kinetics (rate measurements) and mechanisms (product measurements) of the reactions of various RO_2 with NO; the reactions of NO_3 with various alkenes and the reactions of OH with various $RONO_2$ species. The temperature- and pressure-dependence of such data would also be of benefit.
- The systematic measurement of saturation vapour pressures of a variety of organic nitrogen-containing species (particularly alkyl and peroxyacyl nitrates) would be of benefit in formulating structure property relationships.
- Additional studies of the conversion of NO_2 to HONO on surfaces would be very instructive.
- New experimental designs are needed to study the radical and molecular products of the reactions of ozone with various alkenes in the presence of NO_x.
- Finally, detailed chemical mechanisms such as the Master Chemical Mechanism should continue to develop and evolve with the state of knowledge of the constituent chemistry, and mechanisms should be tested against the best field data available. Additionally, large atmospheric models should be encouraged to incorporate the most up-to-date chemical schemes.

Surface – atmosphere exchange of fixed nitrogen.

This topic is discussed separately in the accompanying paper by David Fowler and colleagues (Fowler
2006).

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Discussion Meeting

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