



Transport and Transformation of Pollutants (T&TP)

ACCENT-T&TP: An ACCENT Joint Research Programme

Frontiers in the Transport and Transformation of Pollutants

The Report of the Barnsdale Expert Meeting, 2004

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1. Executive Summary

The Barnsdale Expert Meeting on Frontiers in Transport and Transformation of Pollutants was the first workshop of the newly formed T&TP project, one of the four jointly executed research programmes of ACCENT (<http://www.accent-network.org/>). The purpose of the meeting was to review the state of understanding in four key research areas and so produce recommendations for future activities for ACCENT-T&TP.

Each the four working groups identified a variety of key issues in their respective areas and made a number of recommendations for future activities within T&TP and in ACCENT, which are summarised below.

Group 1: Chemical Complexity

The group recommended the following.

- a. Formation of an expert group on the **nitrogen cycle** with the aim of writing an overview paper – to be led by *David Fowler*.
- b. Preparation of a summary of the main uncertainties in the formation of SOA (**secondary organic aerosol**) from the gas phase – to be led *Michael. E. Jenkin*.
- c. Compilation a catalogue of past and upcoming campaigns (on website) to promote interactions.
- d. To "add value" to future campaigns by enabling complementary measurements for enhanced system understanding, in particular between gas phase, aerosol, nitrogen cycling, biological and deposition groups.
- e. To facilitate visits and meetings between disciplines.
- f. To encourage MCM - aerosol developments.
- g. To assimilate the knowledge from past chamber experiments and make it more accessible to scientists.

Group 2: Long-range Transport of Pollutants

The group recommended the following.

- a. Existing data that could be used to examine LRT should be collected together to create relevant database. A workshop including participants from previous EU projects (*e.g.* TRADEOFF) and data centres as well as end users should be the first step to formulating a strategy to achieve this. T&TP or the ACCENT Data Task might then be able to provide the resources required.
- b. A workshop would be useful to identify measurement requirement (where, what, frequency of measurements). This could be linked to IGACO. ACCENT could provide support through the Infrastructure Task.
- c. A workshop to plan an Arctic experiment which would bring together experts in Arctic research and experts in LRT.
- d. Encourage interaction with the ACCENT Aerosols Activity, which can provide much advancement in the characterisation of aerosols, the ACCENT Modelling Task which could provide improvements in modelling techniques and the ACCENT Emissions Activity which should provide improved model inputs.

Group 3: Chemical Weather

The group recommended the following.

- a. Organisation of a workshop or similar meeting with discussion groups on chemical weather. It would probably be wise to choose a subset of the issues discussed within the group to focus on at such a workshop, now that this group has taken the task of defining the overall framework.
- b. Surveying the atmospheric sciences community to develop a listing of the currently operational (and “standby”) chemical weather forecast systems, subdivided into types (by scales and applications). A website with such a catalogue including links to the various operational systems would probably be of great service to the community.
- c. To link, *via* T&TP, with the chemistry-climate group to define metrics, as well as provide a mechanism for linking to the public in terms of understanding the relative value of different metrics (*e.g.* PM levels, visibility, *etc.*).

Group 4: Chemistry and Climate Interactions

The group recommended the following.

- a. A model experiment on **convection** (*David Stevenson*); to elucidate:
 - how changing climate will affect convection;
 - the impact of NO_x emissions from lightning: and
 - the impact of convection on chemistry.
- b. A workshop on the **nitrogen cycle** (*David Fowler*); (see Group 1)
- c. A model experiment on **natural variability**, studying, perhaps, the El Nino/ La Nina phenomena, or the North Atlantic oscillation. There are possible links here to the RETRO project led by *Martin Schultz* and also AMMA.
- d. To cooperate on **emissions** with the ACCENT - emissions/GEIA group led by *Claire Granier*.
- e. **Aerosols**: To cooperate in the completion of the AEROCOM exercise in 2005 in evaluating and reducing uncertainties in the aerosol direct climate effect (*Hans Feichter* and *Frank Dentener* are the contact persons).
- f. To explore the area of **multiphase chemistry** with a view to it being an ACCENT topic since it appears to be of increasing interest. (*Maria Kanakidou*)
- g. **Metrics**: An effort should be made to define better and more representative metrics of climate change, air pollution and hydrological cycle perturbations that will also provide regional information (*Ivar Isaksen* and *Frank Dentener* are the contact persons).

The T&TP steering group will review all these recommendations and decide with which to proceed. The recommendations will also be brought to the attention of the ACCENT community.

2. Introduction; ACCENT - T&TP

2.1 Air Pollution

Air Pollution has a direct effect on the quality of life on earth. Its first manifestations were recognised officially in Roman times with regulations curbing the activities of certain trades. Now, with the increases in population and in agricultural and industrial activities in the nineteenth and twentieth centuries, it is all pervasive, showing itself in:

- the global decrease in stratospheric ozone and the attendant increase in surface ultraviolet radiation, emphasised by the ozone hole appearing over the Antarctic;
- the occurrence of summer smog over most cities in the world, including the developing countries, and the increased ozone background in the northern troposphere;
- the increase in greenhouse gases and aerosols in the atmosphere and associated climate change;
- acid rain and the eutrophication of surface waters and other natural ecosystems by atmospheric deposition;
- enhanced aerosol and photo-oxidant levels due to biomass burning and other agricultural activity;
- the increase in fine particles in regions of industrial development and population growth with an attendant reduction in visibility and an increase in human health effects;
- the long range transport of air pollution to regions far from the industrial activity; and
- the appearance of semi-volatile persistent organic compounds and heavy metals in hitherto pristine regions far from their sources.

Many of these changes in atmospheric composition have adverse effects on human and ecosystem health, on water supply and quality, and on crop growth. A variety of abatement measures have been introduced or considered to reduce the effects. However, continued growth in human activities, to expand economies and to alleviate poverty, will ensure that these effects continue to be of concern for the foreseeable future.

Air pollution involves the aerial transport of pollutants between the emission source and the sites of deposition as well as the chemical transformation of the pollutants in the atmosphere. Not only are pollutants and trace substances chemically removed by atmospheric processes, they can also be transformed into secondary pollutants; an example here is surface ozone which results from the reaction of nitrogen oxides and hydrocarbons in the presence of sunlight. Thus, air pollution combines the complexity of meteorology with that of atmospheric chemistry and, while we have a reasonable overall picture of the situation, the details, on which forecasting and analysis depend, are far from clear.

2.2 T&TP Aims

The aim of ACCENT T&TP is to bring together the European community of researchers concerned with atmospheric chemistry in order to pinpoint the current problems of understanding and to foster research work aimed at resolving the principal difficulties so that the models used for analysis and forecasting on global, regional and local scales are more precise and reliable.

T&TP intends to fulfil the aim with a series of scoping workshops which will take place during the initial period of the program to prioritise key issues (with the aid of policy makers), define an integrated strategy for research on this topic and to plan coordinated activities to tackle nominated research topics. The goal will be to develop a series of scientific sub-foci for this activity, work on which will be pursued in the later stages.

An underlying aim is to coordinate European research efforts in this area and so provide lasting structures for information exchange between research communities, and between the research community and those responsible for environmental policy development.

2.3 T&TP Activities

In order to fulfil the prime objective of this structuring activity a range of workshops/symposia are planned to prioritise of key issues for development of an integrated strategy; to plan future research activities in this area (*e.g.* export of European pollutants to the global atmosphere); and to develop structuring foci

The workshops are to be of a variety of styles, from focused small group interactive workshops to larger community undertakings. The ultimate aim of the workshop series being to arrive at lasting structures for communication and information exchange between the communities and for a set of specific recommendations for research strategies optimized to produce results to be formulated. Special attention will be paid to the role of young researchers and scientists from accession countries in such activities.

Coupled to the scoping activities, a concurrent data collection activity will be undertaken to gather meta-data on the activities of the EU member/accession countries in this science area. This activity is required in order to understand the scope of the co-ordination/exploitation required. Building structures for communication underlines the need for the actual information that is to be exchanged. Researchers in any particular country are often unaware of work being done in another country under the auspices of a national program. In order to overcome this problem, a compilation of national programmes related to T&TP that are of interest to all of the communities will be created. The T&TP national programme information service (NPIS) should act as a focus for exchange of scientific ideas and programmatic.

3 Current issues at the Barnsdale Expert meeting

The Barnsdale Expert Meeting was the first of the T&TP workshops and was focussed on the overall subject itself: *Frontiers in Transport and Transformation of Pollutants*. The T&TP Steering Group chose four topics to concentrate upon:

- Chemical Complexity;
- Long-range Transport of Air Pollutants;
- Chemical Weather; and
- Chemistry and Climate Interactions.

Each of the invited experts in each group was invited to contribute in "voxboxes" – brief presentations illustrated with one or two slides (see the briefing sheet, Appendix C), and to provide in addition a brief report on their contribution to T&TP. The group leader and the rapporteur were expected to guide the group to produce material for a presentation at the plenary session on the results from the group, and a written summary of the main points emerging from the discussions, suitable for publication in the meeting report (see the briefing sheet, Appendix D).

It was hoped that the outcome of the meeting would be a set of four review articles to be published in the literature on the group focus topics. These should review the current state of each field, highlight and elaborate the scientific problems and outline the future directions the field is likely to take. An additional section on the realistic policy applications and environmental impact would be most valuable.

The present report gives the written outcome of the work in each group together with the recommendations for the future of the respective areas and possible future actions for T&TP. The contributions from individual experts are included.

4. Chemical Complexity

Prepared by *Johnathan Williams*

4.1 Participants

Andreas Volz-Thomas (Discussion Leader), Jonathan Williams (Rapporteur), Tony Cox, David Fowler, Sandro Fuzzi, Michael Jenkin, Alistair Lewis, Michela Maione, Paul Monks, Nicolas Moussiopoulos, Mike Pilling, Andre Prevot, David Simpson and Vidmantas Ulevicius

4.2 Introduction

The initial discussion focussed on examining how each participant had interpreted "chemical complexity". The scientists named above all brought several overheads and presented their view on the session's theme. The aim of the initial discussions was to pool the thoughts of the participants in order to define key areas for the remaining discussion. The following subjects were presented in the initial voxbox session:

- VOC – Complex mechanisms, uncertainties, deposition;
- Aromatic compound oxidation uncertainties;
- The Nitrogen cycle, *i.e.* deposition, organic nitrates, night-time chemistry including heterogeneous reactions;
- The complexity of organic carbon (OC) on aerosol, relationship to gaseous precursors;
- Heterogeneous reactions including polymerisation;
- Interaction with biology, emissions and uptake;
- Regional modelling of gases and ultra-fine particles;
- Halocarbons and their role in determining global OH;
- Urban scale processes and turbulence and a consideration of timescales in processes; and
- The dependence of ozone production efficiency on chemical complexity.

All presented chemical systems were deemed complex as there were important aspects of these research areas that could not be fully explained within the framework of current understanding.

4.3 Main Discussion

Three recurring themes emerged from the initial session:

- 1) volatile organic compounds (VOC);
- 2) the nitrogen cycle; and
- 3) aerosol interactions.

For each of these research areas the discussion was driven to answer the following two questions.

- 1) How complex or detailed must our measurements and models be in order to gain improvements in system understanding (qualitative and quantitative)?
- 2) How can we most effectively proceed to investigate chemical complexity?

4.3.1 Volatile Organic Compounds

The virtually unlimited number of possible organic species and potential photochemical products makes this theme inherently complex. Already, the explicit description of the oxidation of a simple molecule such as pentane to CO₂ and H₂O, leads to an enormous number of reactions and intermediate products. Circa 5000 species can be generated by a mechanism generator for pentane even when compounds representing less than 1% of the starting species are ignored. It was also noted that tens of thousands of species have been identified in the air we breathe by techniques such as comprehensive gas chromatography. Figure 1 shows a measurement of C5 - C15 hydrocarbons in ambient air, where each point indicated represents one (or more) organic species.

The Master Chemical Mechanism (MCM), the presently most advanced gas phase mechanism, contains 124 VOC species which are oxidised to CO₂ in 14000 gas phase reactions. Of the 650 species in the UK emission inventory the MCM covers 70 % either explicitly or as surrogates. The question was then posed as to how successful can a reductionist strategy be? Is it possible within reason to summarise the effects of hydrocarbons in a few simple equations? This was shown to be feasible when focussing on simple issues, such as ozone production. Modelling of regional ozone production seems to produce realistic results relatively independent of the degree of VOC speciation, provided that key quantities, such as total reactivity are realistically parameterised. It was generally agreed, however, that explicit or complex approaches are needed for scientific studies in order to take account of all available knowledge, whereas parameterised models are only useful for the limited purpose they had been constructed and tested for. New problems should be examined using models that encapsulate the state of the art understanding rather than an artificial model scenario. It was concluded that reality is complex and that complexity should not be avoided in research. It was agreed that the MCM is an excellent tool for examining chemical complexity despite there being many areas where improvement is needed in the scheme (*e.g.* organic nitrates, organic hydroperoxides, long chain alkanes, and short lived species).

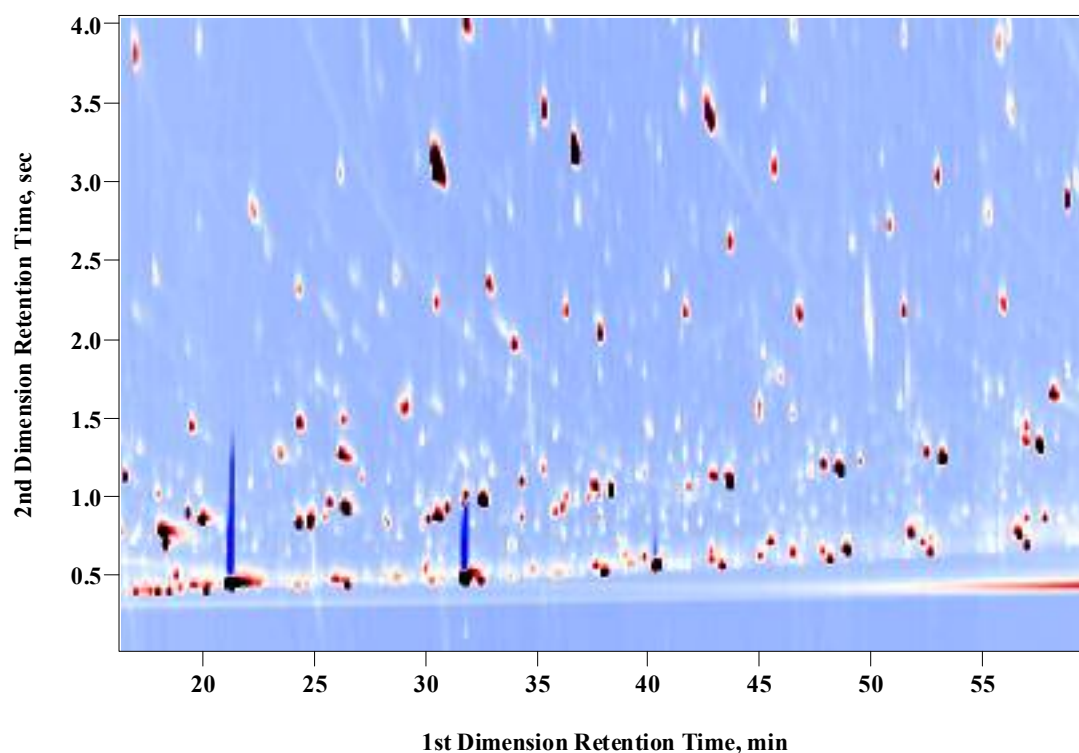


Figure 1. Two dimensional gas chromatograph of ambient air showing the C5 - C15 hydrocarbons. Each point indicated represents one (or more) organic species. (Unpublished data J. Williams)

Polyols and other multifunctionals were given as examples of species at trace concentration with complex formation mechanisms but which have profound effects in the atmosphere, namely nucleation.

A strong limitation in most chemical mechanisms is their limitation to gas phase chemistry. Missing aerosol formation and interaction processes, as well as missing/unknown interaction with the biosphere and deposition in general may be important factors why models presently fail to reproduce several key measurements, such as formaldehyde or radicals, under some circumstances. However, it was recognised that unwanted complexity, in the form of measurement interferences, may also be an obstacle in improving system understanding. In this sense, it is important to maintain the balance between the complexity needed for properly describing the system under investigation and the possibility of obtaining "ground truth" from measurements.

It was the opinion of the group that for policy making, simpler models must be developed that have been shown to match the simulation capability of the explicit models.

4.3.2 Nitrogen cycle

As in the VOC discussion it was shown that the nitrogen cycle is revealing itself to be more complex than previously thought. Nitric acid measurements were shown to have decreased by only 10% in the United Kingdom despite a 50% reduction in NO_x emissions.

It was also pointed out that current NO_3 and O_3 measurements cannot be reconciled by gas phase reactions and the discussion highlighted the importance of the heterogeneous hydrolysis of N_2O_5 for the nitrogen budget. Another example for the importance of surface reactions in adding complexity to the nitrogen cycle (and to the HO_x radical budgets) was HONO. In the course of the discussion, it was stated that for ozone prediction models getting NO_x right was more important than increased VOC complexity. It also was noted that, similar to the VOC discussions, increasing the scope of this research to neighbouring

fields such as the biosphere, ocean, aerosols could help in the elucidation of current irresolvable measurement phenomena.

Nota bene, in the subsequent rapporteur sessions Dr Hanwant Singh pointed out that a session entitled "Chemistry at the Interfaces" had been proposed for the 2006 IGAC meeting in Cape Town.

Since fixed nitrogen is in most ecosystems the limiting factor for primary productivity the nitrogen cycle has important links to the carbon cycle and possibly VOC emissions as well. It is therefore particularly important to assess. It was identified that there is a need for an overview article in this field embracing the knowledge of the various areas influencing nitrogen cycling.

4.3.3 Aerosols

Aerosols were recognised as an extremely complex field in chemical terms. Recent works have shown the enormous complexity of organic matter on aerosol, with important links to biological sources. Liquid phase reactions were considered more complex (being reversible or pH dependent, or surface activated) and the aerosol composition even more complex and variable than the gas phase. In addition it has recently been shown, both in the laboratory and ambient air, that polymerisation is occurring between organic molecules on aerosol surfaces. Molecules with a mass of around 800 amu can develop from small compounds on the aerosol surface even in the absence of light.

It was considered that the full complexity of organic aerosol would be extremely difficult to model explicitly. The functional group approach was suggested as a promising alternative because it provides scientific means of relating model results to measurable quantities such as total carboxylic acids, or total alcohols, which are important for better understanding the secondary effect of aerosol on the Earth's radiative budget. A strong overlap was recognised between the fields of aerosol and VOC, as well as biology.

4.4 Conclusions

The general conclusions of the discussions were as follows.

- 1) Complexity cannot be avoided, because reality **is** chemically complex. This is especially true for aerosol and VOC related research.
- 2) Increased complexity is needed for improved system understanding, but increased emphasis should also be placed on interfaces and research should not be isolated to one phase. The links between the different issues and interfaces identified are shown schematically in Figure 2.
- 3) Policy applications need simple but accurate expressions that must be tested for the purpose against more complex mechanisms.
- 4) The functional group approach developed for SOA (secondary organic aerosol) is very promising, both for measurements and models.

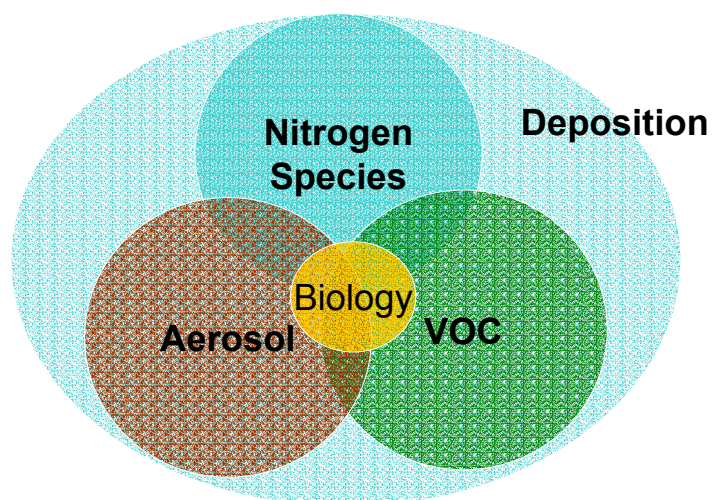


Figure 2. The overlap between the various areas of interest.

4.5 Action Items and Initiatives for ACCENT

From the discussions in the chemical complexity session, the following actions were found to be of immediate importance.

- 1) Founding of an expert group on the nitrogen cycle with the aim of writing an overview paper – to be led by *David Fowler*.
- 2) Preparation of a summary of the main uncertainties in the formation of SOA from the gas phase – to be led *Michael. E. Jenkin*

It was further proposed that to support research related to T&TP effectively, ACCENT should try to:

- 1) compile a catalogue of past and upcoming campaigns (on website) to promote interactions;
- 2) "add value" to future campaigns by enabling complementary measurements for enhanced system understanding, in particular between gas phase, aerosol, nitrogen cycling, biological and deposition groups;
- 3) facilitate visits and meetings between disciplines;
- 4) encourage MCM - aerosol developments; and
- 5) assimilate the knowledge from past chamber experiments and make it more accessible to scientists.

5. Long-range Transport of Pollutants

Prepared by *Claire Reeves*

5.1 Participants

Kathy Law (Discussion Leader), Claire Reeves (Rapporteur), Isabelle Bey, Hugh Coe, Kosta Ganev, Claire Granier, Heidi Huntrieser, Maarten Krol, Paolo Laj, Jose Luis Palau, Stuart Penkett, Petra Siebert, Hanwant Singh and Thomas Trickl.

5.2 Introduction: Six topics within LRT

Prior to the meeting the Discussion Leader and Rapporteur had come up with 6 topics for discussion to which participants were asked to tailor their voxboxes. The discussion was thus made up of several voxbox presentations and general discussion on each topic.

Topic 1: What is the observational evidence for LRT of oxidants and aerosols in different regions and altitudes?

Numerous examples of observations of LRT were presented. Distinct plumes of pollution from North America were observed over the Atlantic in several field experiments (*e.g.* ACSOE, ICARTT), and over Europe (*e.g.* EXPORT, CONTRACE (Figures 5.1 to 5.3)). Correlations of NO_y with C_2Cl_4 at Mace Head showed the NO_y not to be of stratospheric origin. CO/NO_y ratios in CONTRACE indicated the age of the pollution to be 4 to 5 days in agreement with O_3 plume leaving the north York area as observed by MOZAIC. EARLINET lidar in Garmisch has observed dust from the Sahara and aerosols from Canadian forest fires. CARIBIC flights from Europe to the Caribbean observed a widespread increase in O_3 , aerosols and halocarbons between 35 – 40 °N in the upper troposphere (UT).

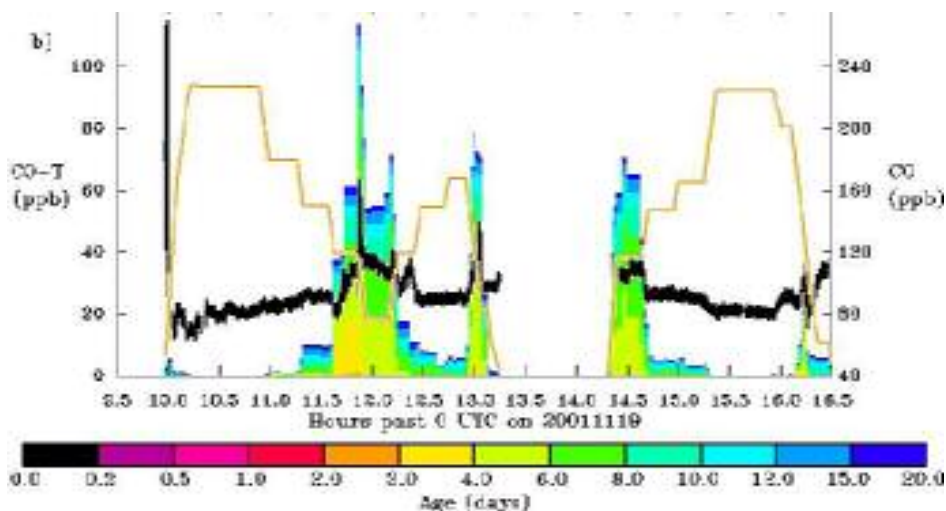


Figure 5.1 Age spectra of the North American CO Tracer and Falcon measurements from 19th November 2001. FLEXPART North American CO Tracer (colour), Falcon CO (black), Falcon altitude (brown).

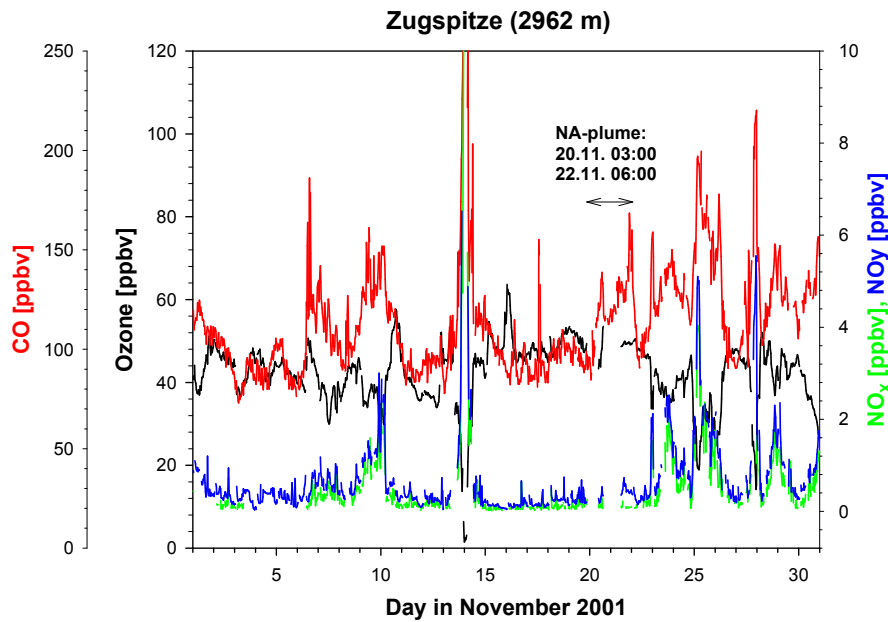


Figure 5.2 Time series of trace gas concentrations at Zugspitze, showing North American pollution on 20th-22nd November 2001.

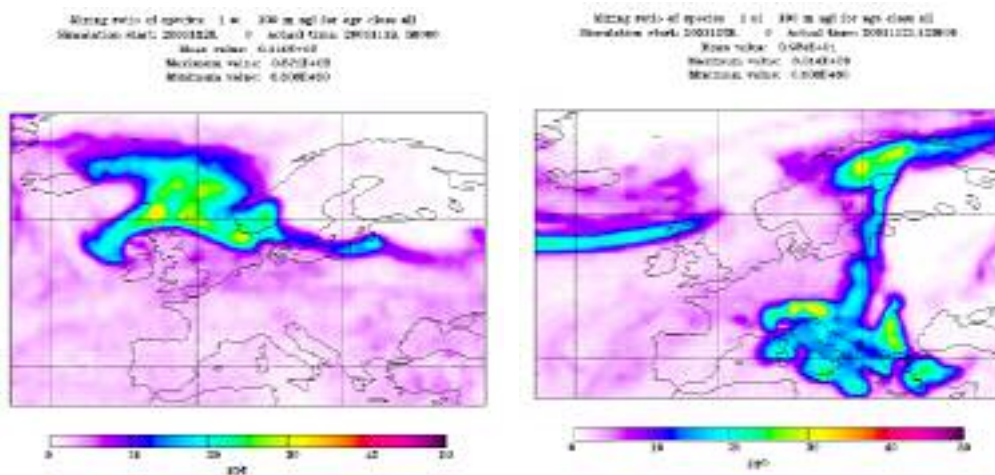


Figure 5.3 Evolution of FLEXPART North American CO tracer over Europe:
Left: 19th November 2001, Right: 21st November 2001.

The ICARTT experiment in the summer of 2004 provided much observational evidence of extensive long range transport of pollution from North American forest fires. Large volumes of the troposphere over the North Atlantic had enhanced CO concentrations and visibility was often very poor due to the smoke. In addition, there were some very narrow filaments with extremely high CO concentrations. HCN, a product of biomass burning, was observed to be high in these plumes, clearly indicating that they originated from the forest fires. PAN, a secondary pollutant, was also observed to be elevated in concentration, but O₃ was often not enhanced greatly. The chemistry leading to this signature in the secondary pollutants requires further examination. Below the forest fire plumes North American anthropogenic pollution was often observed and pollution from Asia was also observed on many occasions over North America. In the UT the filaments of pollution were often seen to be intertwined with stratospheric air. Satellites observations clearly showed the smoke plumes (MODIS), but validation of vertical profiles of CO from AIRS by *in-situ* aircraft observations show that advancements are still required in the analysis of remote sensing data from satellites.

Two papers have recently been published discussing the chemical and physical characterisation of aerosols over Europe from different source regions.

There was some discussion of the use of trajectories in the study of LRT. It is clear that several previous studies have provided much evidence of the accuracy of trajectories allowing them to be used with confidence for synoptic type of air flow. However, their limitations must be recognised, in particular in convective situations. Much advancement is being made to “trajectory” type models such as FLEXPART which includes convection, turbulence, wet and dry deposition, which allows better determination of emission regions.

Topic 2: Are we able to quantify the net photochemical production/loss of oxidants (O₃, HO_x, etc) along different LRT pathways (e.g. LT/PBL, UT, through clouds)?

There is now quite a lot of information on the net photochemical production rate of O₃. However this is largely from case studies and the results need to be integrated. It is still not clear where all the O₃ is being made. The lifetimes of O₃ and NO are higher in the UT than boundary layer. How much O₃ gets out of the boundary layer? Case studies have been done on, for example, mountain venting rates, but more climatological work required.

With regard to modelling changes of O₃ in plumes, there is the complexity of mixing. A case study from NARE/ACSOE (11th Sep – 14th Sep 1997 (P3 to C-130)) shows that agreement between modelled and measured rates of change of various trace gases (CO, O₃, PAN and NO_x) differs between gases depending on the amount of mixing invoked. Models need to include better representation of mixing processes. Some questions posed were:

- What model developments are required?
- Chemistry in transport models?
- Adaptive grids?
- Combination of grid and particle modelling?

There are still some difficulties in measuring and modelling HO_x-NO_x cycles. Measured HCHO in the UT is often at much higher concentrations than expected from its modelled lifetime of a few hours. We therefore do not fully understand its chemical production. Modelled and measured concentrations of HO₂NO₂ are often very different. N₂O₅ has been observed to be very high in concentration at night (up to 500 pptv in the north York plume). Essentially the areas requiring further work are VOC and night-time chemistry. In addition there are many unknowns with regard to heterogeneous chemistry (not discussed here). To improve our understanding of much of this chemistry more accurate measurements are required.

Topic 3: What are the main processes governing LRT of aerosols (formation, evolution, loss)?

Existing knowledge of LRT of aerosols is sparse. Data on the chemical composition of the aerosol is also very sparse. Recent data on the mass spectrum and functionality is becoming available from aerosol mass spectrometers. This, however, focuses on the composition of the core, where the mass is, and not the surface characteristics, which can have a large impact on the aerosol's physical characteristics (e.g. CCN properties). During LRT the particle mass and properties are modified (e.g. radiative, surface characteristics, lifetime and scavenging).

Oxidised organics are ubiquitous. They are internally mixed with sulphate, but the complexity is unresolved. Aerosol organic carbon formed by secondary processes dominates the load. The processing and nature of this material is similar throughout the continental NH. During ITCT 2k2 (west coast of California) the aerosol lifetime was found

to be 4 to 5 days. Heavily oxidised material has been found to correlate well with secondary gas phase pollutants (e.g. aldehydes).

Most of the air in the mid to UT has gone through cloud and therefore much aerosol has been washout. However, precursors such as DMS or SO₂, may still exist. We need to know more about where the aerosol is generated, how it grows and where it is transported. For example, is the aerosol in the MBL due to sea salt or sulphate aerosols descending from aloft?

During ITOP/ICARTT 2-6 mg m⁻³ of sulphate and organic aerosol was observed over the mid- Atlantic. This is similar to levels in the rural UK. SO₂ concentrations in the UK have decreased considerably over recent years and yet sulphate aerosol records from 1997 to 2002 at Eskdalemuir, Scotland have not shown a similar decline. Why? Is the sulfate coming from LRT? Has the oxidising capacity of the atmosphere changed?

There is now considerable evidence of LRT of mineral dust. Dust can have a direct radiative effect, can be converted to CCN and provide an input of iron and other trace elements to the oceans. It can also act as a sink for HNO₃ leading to reduced O₃ levels.

The question of the impact of biology on aerosols was also raised.

Much more data is required, but what should the measurement strategy be? Which sites? Links with EMEP? What frequency? (Chemical analysis is very expensive). What can be provided by the ACCENT Infrastructure Task and the Aerosol Activity?

Topic 4: What are the relative contributions of in-situ emissions (aircraft, lightning, ships) and surface anthropogenic/biogenic emissions to aerosol and oxidant formation during LRT?

There have now been a number of studies by DLR examining the NO_x budget in the UT over Europe, the North Atlantic and Brazil, in particular the sources from aircraft and lightning. There is also observational evidence of emissions from ships affecting NO_x concentrations along the N. Sea coast. Large amounts of sulphate aerosol have been observed in the Bristol Channel.

Model studies suggest that lightning and Asian emissions have a similar size impact on the O₃ over the Mediterranean. Also considerable O₃ is transported from the North American BL to UT over the Atlantic, little extra O₃ is produced on route, much less than that produce by in-situ aircraft emissions of NO_x. However the ability of models to simulate the impact of plumes on regional chemistry was discussed as being an important issue (i.e. the non-linearity of chemistry and mixing).

There was much discussion about the development of source-receptor techniques (inverse modelling and adjoints), with regard to quantifying the contribution of different source regions to observed pollutant distributions. What are the model and measurement errors? Can this be done for secondary products (e.g. O₃ and aerosols)?

Topic 5: What is the contribution of LRT to background air quality and ecosystems (transport patterns, wet/dry deposition etc.)?

Quite a lot of evidence was presented for LRT of pollutants (CO, O₃ and aerosols) to the free troposphere (FT) over Europe. This includes data from lidar at Garmisch and Zugspitze, aircraft and mountain sites such as Zugspitze (See Figure) and Arosa. There is evidence of background concentrations of O₃ increasing at sea level sites on the west coast of Northern Hemisphere continents (e.g. Mace Head, Ireland and Quillayute, WA), but there is not much information on the contribution of LRT to back ground air quality.

As well as intercontinental there is also intra-continental LRT of pollutants and examples of recirculation were presented. *i.e.* polluted air from Europe being exported out over the North Atlantic and then being re-imported, and air being re-circulated in the Mediterranean basin over several days.

On the whole O₃ was considered not to be a good tracer of LRT because it is not a primary pollutant and thus is an integral of the chemistry. Also O₃ can come from the stratosphere and a number of examples were presented of filaments of LRT pollution mixing with stratospheric air in the UT.

Topic 6: What is the net impact of LRT on climate change (GHGs, halons, aerosols) and how will LRT be affected by climate change (transport patterns, background pollutant levels, dry deposition)?

LRT redistributes radiative gases to areas of different sensitivity. The source of O₃ is not fully quantified, thus the impact of LRT on O₃ is still not well known. For aerosols the direct effect can be more easily quantified, but LRT changes the aerosol radiative and CCN properties.

The impact of climate change on LRT is largely unknown, but it is expected (*e.g.* emissions from lightning, weather patterns). How can we determine if observed changes are due to climate change? Can we analyse past variability? Currently much of the work in this area is theoretical modelling and there are few observational constraints. This whole issue is a major challenge for the future.

5.3 Outcome and Future Directions

It was decided that there was no need for another review paper, due to a couple of recently published papers and a book edited by Andreas Stohl. Also the EXPORT-E2 report contained many recommendations. However the aim is to publish a “new directions” type article (*Atmos Environ*), although the value of this is still being investigated. This will be a short 2-3 page article to identify gaps in recent reviews (*e.g.* aerosols), focus on impact questions such as on air quality, future directions in collation of existing data, measurement strategy (field & routine) and modelling/data analysis (*i.e.* what is needed to make real progress?).

5.4 What should T&TP and ACCENT do?

- Much data already exists that could be used to examine LRT. However this needs to be collected together to create relevant database. A workshop including participants from previous EU projects (*e.g.* TRADEOFF) and data centres as well as end users should be the first step to formulating a strategy to achieve this. T&TP or the ACCENT Data Task might then be able to provide the resources required.
- A workshop would be useful to identify measurement requirement (where, what, freq. of measurements). This could be linked to IGACO. ACCENT could provide support through the Infrastructure Task.
- There was a recommendation for a workshop to plan an Arctic experiment which would bring together experts in Arctic research and experts in LRT.
- The ACCENT Aerosols Activity can provide much advancement in the characterisation of aerosols.

- The ACCENT Modelling Task can provide improvements in modelling techniques. Improved access to model products would be useful for LRT research.
- The ACCENT Emissions Activity should provide improved model inputs.
- To lever funds the ACCENT Policy Task could provide assistance with recommendations for policy relevance.

6. Chemical Weather

Prepared by *Mark Lawrence*

6.1 Participants

Oystein Hov (Discussion Leader), Mark Lawrence (Rapporteur), Matthias Beekman, Joergen Brandt, Hendrik Elbern, Henk Eskes, Hans Feichter and Masayuki Takigawa

6.2 Introduction

The chemical weather (CW) discussion group settled on a set of key questions characterizing what chemical weather research is and what major issues need to be addressed in current and near future research. For each of the questions, we defined a set of either initial answers or further sub-questions to help guide the community working on this topic, and to help us to relate to other atmospheric research communities. We do not feel that the topic of chemical weather is mature enough yet for a full-blown review paper, though it may be within a few years, given the explosion of activity, especially in chemical weather forecasting at all scales. Our intention is to refine this summary into a short paper to submit for publication in a forum like Atmospheric Environment's New Directions.

The term "chemical weather" has only come into use in the last few years. It is unclear who coined it, or when (though probably around 2000), but its use has clearly exploded, at least in informal settings. A search on "chemical weather" with Google reveals over 5000 entries. On the other hand, "chemical weather" in the Web of Science only reveals 9 entries, only three of these in the titles of papers (Lawrence *et al.*, 2003; Uno *et al.*, 2003, 2004; the rest are in the abstracts), so it has not yet taken off in its use in formal, peer-reviewed literature.

6.3 What is the chemical weather?

The first task taken by the group was defining what is actually meant by the term:

The working definition settled on by the group is:

- Local, regional and global distributions of important trace gases and aerosols on time scales of minutes to hours to days, particularly in light of their various impacts, such as on human health, ecosystems, the meteorological weather and climate.

The chemical weather can be seen as analogous to the meteorological weather, and can be contrasted with the chemical climate, which are mean trace gas and aerosol distributions on timescales of months to decades. In particular, chemical weather emphasizes the strong influence of meteorological variability - and the chemical response to this variability - on air quality.

It is important to note that "chemical weather" is not just a catchy new term to describe the same old research. It is recognition of the myriad 2-way connections between atmospheric chemistry and meteorological weather, knowledge of which grows as our understanding of the depth of chemical complexity and the variability and fine structure of transport and

removal processes in the atmosphere continues to evolve. It is also a recognition of the importance of short-term variability, both in governing the long-term climatological state due to chemical non-linearities, and in the tendency for extremes to become more common under anticipated global climate change conditions, and finally in the importance of extremes for health and ecosystems.

Finally, it has been suggested that the term, chemical weather, may evoke distinctly negative associations with the general public; this is in need of further assessment and discussion, as is the use of related terms, such as, air-quality forecasts and analyses.

6.4 Five questions characterizing chemical weather

a. What are the main applications of the study of chemical weather (simulations, forecasts, and monitoring)?

We came up with a rather long list of major applications of the study of chemical weather, including the more “traditional” ones such as human health which have been considered extensively in the past few years, and other possibilities which have not been discussed much yet. These applications are:

1) Human health – Air quality forecasts and analyses

This includes aerosols, O₃, NO₂, and other gases. Both forecasts and analyses of air quality are useful, on the one side for short-term public warnings, and on the other side for scientific assessments of the past health impacts of pollution. It is particularly unclear at present which measures are most pertinent to human health. Which aerosols need to be measured and simulated (PM10 and PM2.5, which have traditionally been focused on, are known to be imperfect indicators for human health)? What levels of various aerosols and gases, integrated over what periods of times, can be considered harmful exposure? Finally, it is important to establish the product of the confidence in these indicators with our confidence in our simulations, so we can determine the extent to which we should allow and/or encourage this to flow into decisions on emissions restrictions.

2) Effects on agriculture and ecosystems

The detrimental effects that pollutants like O₃ and particles can have on crops has been demonstrated, but like the effects on human health the harmful levels of exposure are poorly understood. With respect to chemical weather, we need to assess the importance of short-term variability (*versus* long-term mean concentrations like AOT40), especially when this is considered in correlation with meteorology (*e.g.* soil moisture and humidity determine the degree of stomatal opening, and are also correlated with O₃ levels, which tend to be higher during anti-cyclonic conditions). A further step would be to determine the possible effectiveness of short-term response strategies (*e.g.* strategic irrigation). Finally, this branch needs to be coupled to the extensive research results available on the long-term effects of acid rain (which may also depend strongly on correlations between pollutant levels and meteorological conditions) and eutrophication.

3) Effects on tourism

There are three particular effects that chemical weather has on tourism: 1) air quality, which can substantially reduce the attractiveness to tourists, 2) visibility, which is paramount for tourism in vista regions, and 3) the connection to long-term corrosion damage to buildings, monuments, and other structures. Integrated impact studies of the economic consequences of these factors would probably be quite valuable.

4) *UV forecasts*

Particularly in high-latitude regions there is a considerable concern about the relationship between stratospheric O₃ depletion, UV levels at the surface, and skin cancer. Forecasts and short-term warnings are feasible based on stratospheric O₃ chemical weather forecasts together with forecasts of tropospheric clouds and aerosols. Clear-sky UV index forecasts are already being reported in the media in some countries, which may help to increase public awareness about the harmful effects of UV.

5) *Field campaign planning*

This has perhaps been the most extensive application of chemical weather forecasts to date. A very large variety of models are already providing chemical weather forecasts at local, regional, and global scales, ranging from simple tracers to complex hydrocarbon and multi-type aerosol chemistry, using both Eulerian and Lagrangian frameworks. Some already include assimilation of chemical and/or distributions (which can be valuable, but are not necessary for chemical weather forecasts in the same way as they are for meteorological weather, since the chemical weather system is less chaotic and is driven more strongly by boundary conditions such as emissions, and by the transport vectors, than by initial conditions). In the future, the possibility of ensemble predictions may result in a major step forward, not only for field campaign planning, but for many other applications discussed here as well.

6) *Analysis of observations*

A broader use of chemical weather simulations and analysis is to help place observations of limited spatial and temporal extent in the larger context of the overall regional chemical weather. This applies particularly to field campaign measurements with airborne platforms, but can also be important for surface stations which only sample at a point, and for satellites, which do not sample continuously (and will not until the dream of a geosynchronous atmospheric chemistry satellite is realized).

7) *Improvements in numerical weather prediction (NWP) models*

There are several ways that can already be imagined in which the availability of chemical weather forecasts could help to improve meteorological weather forecasts. One of these is the coupling of simulated aerosols to the cloud microphysics parameterizations to improve precipitation and cloud forecasts. Another is the coupling of the aerosol and trace gas fields to the radiative transfer parameterizations, which in turn influence the radiation budgets and circulation patterns. Yet another example is the use of stratospheric ozone as a tracer for transport, which has been shown to be able to improve the analyses of stratospheric winds. Finally, chemical weather simulations, especially if they are brought into a more operational mode with the availability of regular observations for evaluation in the future, can provide a valuable diagnostic tool for determining the strengths and weaknesses of meteorological analyses (such as successes and failures in predicting intercontinental pollution transport episodes).

8) *Understanding of long-term changes in CW*

Under conditions of global climate change and changing emissions it is certain that both the chemical climate and chemical weather will also change. A lot of study is already going into understanding changes in chemical climate – it will be important to augment this with studies of changes in chemical weather.

9) *Other species, links to other research communities*

Most of our discussions have focused around aerosols and around O₃-related gas phase chemistry. However, there are a wide range of other applications for the study of chemical weather, particularly for chemical weather forecasts, which link in with other research

communities, and which should not be overlooked. These include: POPs, Hg, heavy metals (lead, *etc.*), pollens, accidental chemical releases, radiation leaks, and, sadly, terrorism (chemical, biological, and radioactive).

b. *What are the requirements for chemical weather simulations and forecasts?*

There are four key regulators of trace gas and aerosol distributions which have to be integrated by a model in order to simulate the chemical weather

1) Emissions and Sources

These include anthropogenic, biogenic, and other natural sources (*e.g.* lightning, STE). Important will be eventually including the variability on diurnal, weekly, seasonal, and inter-annual scales, which is not done at present for most types of emissions.

2) Transport

This can be broken down in to a few basic components which are typically simulated individually: winds (advection and diffusion), cumulus convection, BL mixing, and transport in sedimenting (and sometimes lofted and detrained) hydrometeors. In some cases it may be crucial to eventually consider the coupling between various components (*e.g.* the coupling between deep convection and mean vertical upwelling in the Hadley cell).

3) Transformations

Meant by this are chemical reactions and photolysis for gas phase species, and nucleation, coagulation, coalescence, and chemical aging (coating, forming of mixed particles, *etc.*) for aerosols. Simulating this requires knowledge of temperature, water vapour, UV and visible actinic fluxes, oxidant concentrations, aerosols and clouds (in terms of cloud fraction, albedo, and cloud water and ice concentrations)

4) Removal

The simulation of removal of gases and aerosols from the atmosphere depends primarily on information on precipitation (frequency, amount, size distributions, phases (liquid or ice) and vertical origins) and on surface properties for determining dry deposition (land surface type, soil moisture, temperature, ocean surface roughness, near-surface wind speed, *etc.*)

c. *What tools do we have available for studying chemical weather, and how do we best apply them?*

Both models and observations are crucial to the study of chemical weather, and their joint usage in evaluation, assimilation, forecasting, and data interpretation are required.

There are now many models which are providing operational forecasts (taken here to imply routine or regular output which is made readily and quickly available to the community) at local/urban, regional, and global scales. A list of these is beyond the scope of this write-up, but a careful survey of the available systems would probably be of value to the community.

Observations for studying chemical weather can be broken down into 3 subgroups:

- 1) ground-based, including *in-situ* surface measurements (especially long-term monitoring), balloons, and remote sensing;
- 2) air-craft, both in terms of field campaigns and “routine” measurements projects (namely MOZAIC, JAL, CARIBIC, NOXAR); and
- 3) satellite instruments, many of which are already being put to extensive use, such as GOME, SCIAMACHY, OMI, MOPITT, MIPAS, *etc.*

There are several basic purposes for which these observations can be applied. For the direct study of chemical weather, long time series of the most important parameters in regions where their effects are likely to be most important are the key parameters. For chemical weather model evaluation, the main desires are long time series at a variety of locations for the key parameters being delivered and the key precursors thereof. For assimilation into chemical weather modelling systems, the desire is substantial spatial and temporal coverage, good error estimates, averaging kernel information for satellite data, and when used in forecast systems, near real time delivery. Assimilation can be done with data from a variety of sources (ground-based, aircraft, and satellite, as indicated above), with approaches varying from simple (OI) to complex (4-D var, Kalman). Important key future tasks in the realm of assimilation are: assessing the value of assimilating various individual tracers; assimilation of observations of emissions (*e.g.* biomass burning from actual fires); and consideration of the ability of independent datasets are desired for model evaluation which are not being assimilated into the model being evaluated (and for which model output, *e.g.* vertical trace gas profiles, is not being used in the data processing procedure).

A key tool which is needed for the study of the chemical weather is a carefully-chosen set of diagnostics. In developing this, we should consider what are the key hypotheses we want to test for modelling systems. Can we define a set of standards for chemical weather(F) which the systems should comply with, and how do we quantify the modelling performance, and how it changes over time? Are there equivalent parameters to the meteorologist's 500 hPa height and precipitation yes/no indices which are widely relevant and useful for evaluation of chemical weather(F)?

d. How is chemical weather linked with other major disciplines of atmospheric sciences?

There are many links of chemical weather to other disciplines within the atmospheric sciences. The most evident direct link is to numerical weather prediction; we also consider links to other disciplines broken down into the themes of the discussion groups at the T&TP workshop.

The links for chemical weather with NWP models are bi-directional. One direction is highly evident: chemical weather models depend on the output from NWP models for supplying the meteorological driving fields, which are outlined in the section above on requirements. The other direction – use of aerosol and trace gas simulations/forecasts to help improve precipitation forecasts, cloud cover, surface energy budgets, *etc.* – was also discussed above, in the section on applications.

The links to climate change are similarly bi-directional. On the one hand, climate change implies changes in meteorological weather conditions, which will in turn be manifested as changes in the chemical weather. On the other hand, it will be interesting to examine the role of chemical weather in contributing to climate change. This will go beyond the current focus on the effects of changes in the mean chemical state of the atmosphere (*i.e.* the chemical climate), and consider aspects such as the influence of nonlinearities in aerosol-cloud-climate interactions and nonlinearities in oxidant chemistry and GHG levels (such as the CH₄-OH and NO_x-O₃-OH feedbacks).

Long-range transport has important effects on local chemical weather; a considerable effort has gone into quantifying these effects, particularly for international and intercontinental transport. In the future, careful analyses of chemical weather may in turn be useful as a tool to diagnose and study long-range transport. In doing so, it will be important to keep in mind the role of vertical transport, both in terms of deep convection, which is highly stochastic, and has large effects on short time scales, as well as BL mixing, which is

crucial to determining surface concentrations, and is still very uncertain in chemistry-transport models.

Finally, although much of the study of chemical weather has focused on O₃, CO, NO_x, and basic aerosol types (typically in terms of external mixtures), understanding chemical complexity clearly contributes to our ability to accurately quantify these and other aspects of the chemical weather. It will be important to examine the role of the oodles of VOCs, halogens, and other oddities which are being explored in laboratory and field studies, and to assess the uncertainty in CW simulations which results from the uncertainty in reaction rates and photolysis rates, especially multi-phase processes, and poorly understood aspects of the aging of aerosols (such as polymerization).

e. What are the critical issues for short-term development of CW simulation capability, and where is CW forecasting going in the longer-term future?

We put together a list of some of the issues which we as a group consider to be the most important for guiding near-future research. We do not claim this to be comprehensive, and have made no attempts at prioritizing it, yet.

The key needs we have identified are:

- A careful study of the way that errors in NWP models transfer into errors in CWFs (and how inconsistencies between the setups influence the CWFs);
- Assessment of the resolution and model complexity (chemical speciation) required for various applications, the value of nesting, and the improvement/convergence of results upon model and grid refinement;
- Assessment of the tradeoffs between different approaches for simulating urban air quality, in particular physical prognostic deterministic models versus trained statistical models (regression models);
- Assessment of the extent to which emissions datasets are at present sufficient to satisfy the requirements of CW modelling;
- Definition of basic key diagnostics/standards that are used to document the current quality and improvement of chemical weather(F)s over longer times, creative new approaches to evaluating models which go beyond the traditional quick comparisons with means and standard deviations;
- Assessment of the particular needs for future extensions of the observations networks (e.g. MOZAUTO – like MOZAIC, but instead in service measurements of ozone in automobiles/truck);
- A directed discussion on how we bring together the varied communities focusing on different scales of chemical weather;
- An understanding of how we go about encouraging agencies to direct funds towards issues that are not directly the research of scientists involved in chemical weather, but on which chemical weather simulations rely heavily (e.g. NWP, emissions, observation networks);
- A more focused presentation of the research on chemical weather to the scientific community, public and policy makers; this includes coordination of data dissemination and exchange, web interfaces, and the potential for quasi-ensemble forecasts; and

- Consideration of the possibility and the need for including chemical weather (variability) into the integrated assessment models such as RAINS (*e.g.* in terms of transfer functions from emissions via concentrations to impacts).

6.5 A final question

A final question is what T&TP can do in the field of chemical weather analysis and forecasting? T&TP has already done the chemical weather research field a favor in coordinating this gathering of experts to address the issue of defining chemical weather itself and discussing what the current situation and future needs are.

Probably the main future help would be the standard answer for ACCENT – organizing a workshop or similar meetings with discussion groups on chemical weather. That would need a volunteer to lead it (do we see any hands?). It would probably be wise to choose a subset of the issues discussed above to focus on at such a workshop, now that this group has taken the task of defining the overall framework.

A very direct piece of assistance that ACCENT could provide would be polling the atmospheric sciences community to develop a survey/listing of the currently operational (and standby) chemical weather forecast systems, subdivided into types (by scales and applications). A website with such a catalogue including links to the various operational systems would probably be of great service to the community, but it is a relatively thankless job that an individual researcher is unlikely to be willing to take on alone. Could ACCENT make this happen?

Finally, T&TP could, and would continue to, provide a link to the chemistry-climate group in terms of defining metrics, as well as provide a mechanism for linking to the public in terms of understanding the relative value of different metrics (*e.g.* PM levels, visibility, *etc.*). Again, this would require volunteers to coordinate these linkages.

7. Climate and Chemistry Interactions

Prepared by *Maria Kanakidou*

7.1 Participants

John Pyle (Discussion Leader), Maria Kanakidou (Rapporteur), Frank Dentener, Russ Dickerson, Hans Feichter, Claire Granier, Millan Millan, Christina Schnadt, David Stevenson. Additional input from Horst Fischer and Martin Schulz

The Ozone Climate Review published by EU in 2003 and the joint SPARC/IGAC 2003 workshop report on chemistry/climate interactions (IGAC newsletter June 2004) have been considered as starting points for the discussion. The major areas where chemistry interacts with climate were reviewed with a focus on the limitations in their understanding. The topics that require and can benefit from common effort within ACCENT were emphasised.

7.2 Critical improvements required for understanding chemistry

H₂O: Water vapour is a central atmospheric component, affecting energy budget and transport in the atmosphere, clouds and removal of trace gases and aerosols. Its tropospheric abundance should increase in a warmer climate.

- Direct injections of H₂O might impact LS/UT.
- Important both for global and regional climate.

Do we understand the consequences of H₂O changes and the related feedback mechanisms?

Relevant work was presented by *Christina Schnadt* on climate ECHAM4/MEZON model calculations with consideration of GHG and Ozone depletion substances showing a 7-8 % per decade increase in stratospheric H₂O that is mostly driven by CH₄ oxidation.

Convection: Convection can influence water vapour in the upper troposphere. It also affects the lifetime of those species that have longer lifetimes in the middle and upper troposphere than near the ground. The return of air to the lower troposphere is much slower than the convection mechanism. Linked to this topic are the boundary layer dynamics of which the treatment in the models requires improvement to fit the special needs for chemistry.

The following questions have been identified as priority for ACCENT investigations.

- How does convection change due to the radiative forcing caused by human activities? How do different models respond to climate change?
- What is the consequence of such changes on NO_x emissions by lightning?
- Is the change in convection important and correctly predicted by models?
- How uncertain is this prediction?

To address these topics an ACCENT sub-group led by *David Stevenson* will be formed including experts on convection to design a Model Experiment for today's and future climate that will allow:

- evaluation of the current models capabilities in simulating convection;
- evaluation of the deviation between these models in simulating the future changes in the convection; and
- evaluation of the impact of climate changes on NO_x emissions by lightning.

Some insight on this topic was by the work presented by *David Stevenson* who performed climate/chemistry simulations from 1990 to 2030 changing both biogenic (isoprene) and anthropogenic emissions. He compared 2020s simulations with changing and with fixed climate. Convection patterns shifted, with reduced frequency but greater intensity over the tropics and with more convection over middle latitudes. NO_x from lightning showed small internal variability based on Price & Rind parameterization, with less lightning NO_x in the low and middle tropical troposphere and more in the high troposphere, more lightning NO_x has been calculated in the mid-latitudes troposphere.

The role of nitrogen: The nitrogen cycle is an important driving force for chemistry.

- N-cycling in the atmosphere is not satisfactorily understood and simulated in models.
- There is significant involvement in soil chemistry. N-cycle is a link between atmosphere and surface sciences and is of interest for many different communities of competing interests (*e.g.* atmospheric scientists, food economists, etc). ACCENT could facilitate improved contact between these communities.
- Nitrogen emissions are climate sensitive.
 - Climate change will increase the use of fertilizers.
 - NO_x and NH₃ emission patterns are also shifting from developed to developing countries.

- The inventories of NH₃ are more easily constrained by atmospheric measurements.
- There is a need to quantify nitrogen emission from transport (pollution) and evaluate their impact on climate.

Feedbacks of chemistry on climate will be also picked up in the planned IPCC experiment that will allow evaluation of:

- the capability of different models to reproduce observed NO₂ columns; and
- the robustness of nitrate deposition calculations.

As an ACCENT action, a **nitrogen workshop** (led by *David Fowler*) has been proposed to focus on the atmosphere by inviting scientists from other disciplines. UNESCO is also planning relevant activities. This could be joint effort between the chemical complexity group of T&TP and the biosphere-atmosphere activity of ACCENT, as was discussed during the plenary session, and produce a needed nitrogen review paper which will complement the existing reviews on VOC (by *J. Williams*) and on OA (issued from the PHOENICS EU project by *M. Kanakidou et al.*)

New chemistry

- **Halogens:** The importance of the role of halogens in tropospheric chemistry is an open topic. Might or not be important on a global scale. Recent studies indicate that halogen can cause more than 10 % zonal mean decrease in O₃ in the FT (von Glasow *et al.*, ACPD 2004 also J. Pyle's group unpublished data from THALOS EU project, INDOEX studies showed even higher impact of halogens on O₃).
- **What is determining OH?** OH calculations seem a robust result of the models. The models do not seem to produce any threshold for OH levels. However, there are geographic locations (like, for instance, Black Sea) with particular transport characteristics where injections into the atmosphere may have a more pronounced effect than elsewhere.
- **H₂ cycle:** Interest is increasing because of its use in the energy production. *M. Schulz* is submitting a STREP report on this topic.
- **Kinetics as a function of temperature:** Is there a need for further laboratory studies?

7.3 Critical improvements required for understanding transport

- S/T exchange is of recognized importance and largely uncertain. The discussion focused on the importance of transport into the stratosphere via the tropical tropopause layer TTL.
- Convection (*see above*)
- The tropical tropopause layer and tropopause behaviour: TTL is the main gateway to the stratosphere – a zone through which pollutants are slowly moving to the stratosphere. Key points for the chemistry/climate interactions are
 - the residence time of chemicals in the TTL;
 - tropopause height changes linked to shift in jet streams due to climate change; and

- changes in transport through the TTL due to climate change.

Changes in general circulation including tropopause height and transport to the lowermost stratosphere through the TTL are expected to result from climate modifications. Simulations show that a climate with twice as much CO₂ leads to higher tropical tropopause levels, with the consequences for S/T exchanges. Worth mentioning also is the involvement of the Asian Monsoon in lifting and injecting material (pollutants) in the TTL. Although the interest of this topic has been clearly pointed out, no specific ACCENT action has been identified at the moment.

- The position of jets and its variability are also affecting the total ozone columns. Recently, Bob Hudson's study of TOMS data showed a distinction of tropical/mid latitude / polar ozone zones based on total O₃ column and the position of fronts. The latitude until which tropical O₃ regime is extended has been derived from TOMS data for the period 1979 to 2004 on a monthly basis and is varying from about 32 to 45 deg. The changes can explain part of the observed ozone trend. This variability is attributed partly to both QBO and solar cycle.

- **Natural variability:** La Nina – El Nino, NAO *etc* and their effect on chemistry
It has been recognized that to evaluate the robustness of anthropogenic impact calculations, we need to understand the natural variability. For the period of 1990-2002, there seems to be for El Nino a good correlation with O₃ in the LS/UT area (ST exchange). There is a maximum in the STE 6 months after El Nino. Thus, it is a fact that variability of climate parameters exerts major influence on atmospheric chemistry.

In this perspective it is a challenge to understand:

- the natural variability of the composition of the atmosphere, and
- the atmospheric response to the El Nino type climate.

This topic can be addressed by:

- model simulations for permanent El Nino case or for a composite El Nino / La Nina case study;
- analysis of the frequencies of high and low stagnant pressure systems (as metric for climate changes); and
- possible model comparison experiments and comparison with observations.

This can be an ACCENT effort linked to the RETRO – EU project and led by *Martin Schulz*. It can be also linked to the new EU project AMMA (suggested by *Kathy Law* during the plenary session).

7.4 Critical improvements required for understanding emissions/deposition

A number of emission categories have been identified as climate sensitive.

- Biogenic emissions: their importance for atmospheric chemistry is well established and their dependence on climate as well. However many open questions remain with regard to their response to climate change since such changes might induce the predominance of different vegetation species type that might not behave (as gas emitters) similarly to the studied ones. Then the

established parameterisations may not be applicable. Note also the existence of temperature threshold in plant emissions that implies that emissions do not always increase with increasing temperature.

- Stomatal resistance critical for deposition processes, is limited by H₂O availability that is linked to droughts and strongly affected by extreme weather events.
- Wetlands (CH₄).
- Land use changes. SREs emissions scenarios do not provide information on spatial variability – links between the economists and the emission inventory communities has to be established to overcome this problem.
- Biomass burning and fire frequency. This has been the topic of several studies but major uncertainties remain. Additional effort is needed because of the large impact of these emissions on tropospheric chemistry.
- Ocean emissions. In particular those of organics gases (halogenated) and particles (sea-salt and organics) are poorly modelled. Most progress has been made on DMS oceanic emissions. Climate changes affecting water circulation may also impact these emissions.
- Soil NO_x including coupled vegetation effects
- Snow emissions of NO_x, frost flowers, *etc.* These emissions might become important in changed climates.
- NO_x from lightning is linked to convection that is climate sensitive (see above).
- Uncertainties in anthropogenic emissions are large in particular in view of the increasing emissions from the developing countries. This leads to a shift in emission distributions toward the tropics and Asia resulting to different lifetimes of pollutants and different climate impact.
- Links to other research communities is common theme.

There are many issues related to emissions/deposition. In the context of ACCENT, for chemistry/climate modelling the need is for a closer contact (joint meeting?) with the surface emission community. Within the ACCENT emission group led by Claire Granier, there is particular effort on biomass burning, biogenic and anthropogenic emissions (joint meetings).

7.5 Critical improvements required for understanding aerosol/cloud chemistry

This has been the topic of recent review and synthesis papers, a number of topics critical for understanding the impact of aerosol formation on chemistry and climate have been discussed. Here below we focus on some major points of interest:

- Multiphase chemistry leading to particulate mass formation and affecting oxidant levels in the atmosphere is only partially (mainly sulfate formation) incorporated in most global chemistry transport models. Since it started attracting attention it has been identified as a possible focus for later ACCENT T&TP action (*Maria Kanakidou*). Related to multiphase case chemistry is the secondary aerosol formation, knowledge on which has been covered in recent review papers (see for instance Kanakidou *et al.*, ACPD, 4, 5855, 2004 and refs. therein). SOA formation is also linked to biogenic emissions that are recognised as the main precursors of SOA. The importance of natural variability of these

emissions, of the hydrological cycle and of temperature in determining the SOA level variability in the atmosphere has been raised.

- Marine biogenic contribution to OA has been recently identified (O'Dowd *et al.*, *Nature*, Oct 7, 2004) and requires further understanding and development of source parameterisations for incorporation in CTMs.
- Attention has been attracted also on the analytical problems in measuring aerosols (including the BC definition problems) that turn to be a challenge for the experimental community.
- Optical properties of aerosols/Actinic flux change due to aerosol presence and impacts on chemistry
- Indirect effects of aerosols and Cloud Microphysics → high uncertainty parameterisations in the models needs to be improved in climate models
- Additional points raised are climate induced changes in lifecycles of aerosols and changes in Atmospheric Stability due to the presence of aerosols.

Finally the lack of complexity in climate models with regard to gas/particle chemical interactions has been pointed out and a need for development of more interactive chemistry/climate models has been discussed. It has been pointed out that model complexity should be coherent with measurement capabilities.

Model differences/uncertainties in simulating aerosols in the atmosphere and their direct climate impact is systematically evaluated by the AEROCOM model intercomparison exercise that will be finalized in 2005 and ACCENT T&TP is proposed to co-sponsor.

Regional aspects (including air quality/climate):

The group raised the issue of regional impacts and effects. For example, while threshold effects might not occur globally, the impact of local emissions might trigger significant regional change in some climate indicators. In this context the changes reported in the Mediterranean were discussed along with interesting possible experiments. Large, localized emissions from megacities could lead to regional impacts (*e.g.* pollution, aerosol production, *etc.*). The likely shifts during the coming century in global emissions southwards and eastwards are also expected to have important regional consequences. We anticipate that there will be a raised research profile for all these issues.

New metrics for atmospheric composition and climate change?

Although the radiative forcing concept is largely used because of its simplicity, it has been considered that it is not sufficient to describe the magnitude of climate forcings that are much larger on a regional basis. In addition, there is a need for relatively simple diagrams that will link the emissions to the atmospheric composition changes and to climate. An effort will be put on defining better and more representative metrics of climate change, air pollution and hydrological cycle perturbations that will also provide regional information. This should be an action co-coordinated with the IPCC group. *Ivar Isaksen and Frank Dentener* will form a thinking group.

7.6 Chemistry/climate - T&TP – summary of discussion

Attention should be directed towards the importance of understanding the natural variability. A number of possible ACCENT Actions related to chemistry/climate - T&TP have been identified and are summarized below; the potential lead person also mentioned.

Convection : *Model experiment* (David Stevenson)

- How will changing climate affect convection? (link to ENSEMBLE project).
- Link to NO_x emissions from lightning.
- What is the impact of convection on chemistry?

N-Cycle : *Workshop* (David Fowler)

- Nitrogen workshop with focus on the atmosphere but inviting other scientists.
- Profit from IPCC simulations (N deposition and evaluation of NO₂ columns).
- Check forthcoming activities of UNESCO.

Natural variability: El Nino, La Nina, NAO, A model experiment for permanent El Nino or composite El Nino/La Nina forcing, can be linked to the RETRO EU project that is performing inter-annual simulations for 40 year period from 1957 to 1997 based on ECMWF reanalysis and historical emission inventories compiled in the project. RETRO is led by Martin Schulz (link also to AMMA – *Kathy Law*)

Emissions: T&TP Chemistry/climate group will join the efforts organized by the ACCENT- emissions / GEIA group led by *Claire Granier*.

Aerosols: In the near future, ACCENT T&TP chemistry/climate actions should co-sponsor the completion of the AEROCOM exercise in 2005 in evaluating and reducing uncertainties in the aerosol direct climate effect (*Hans Feichter* and *Frank Dentener* are the contact persons).

Might multiphase chemistry (and impact of biogenics?) be a topic of ACCENT action in the future since is a topic that starts attracting a lot of interest in the scientific community (*Maria Kanakidou*)?

Metrics: An effort will be put on defining better and more representative metrics of climate change, air pollution and hydrological cycle perturbations that will also provide regional information. This should be an action co-coordinated with the IPCC group. *Ivar Isaksen* and *Frank Dentener* will form a thinking group. A link for this action with the Chemical Weather group was suggested during the plenary session.

Other Interesting issues discussed:

- new metrics;
- thresholds – extreme events;
- spatial shift in emission distributions → different lifetimes → different impact; and
- Importance of understanding the natural variability

8. Conclusions and recommendations

As the previous sections indicate, the four working groups identified a variety of key issues in their respective areas and made a number of recommendations for future activities within T&TP and in ACCENT. These are summarised in this section.

Group 1: Chemical Complexity

The group recommended the following.

- a. Formation of an expert group on the nitrogen cycle with the aim of writing an overview paper – to be led by *David Fowler*.
- b. Preparation of a summary of the main uncertainties in the formation of secondary organic aerosol (SOA) from the gas phase – to be led *Michael. E. Jenkin*.
- c. Compilation of a catalogue of past and up and coming campaigns (on website) to promote interactions.
- d. To add value to future campaigns by enabling complementary measurements for enhanced system understanding, in particular between gas phase, aerosol, nitrogen cycling, biological and deposition groups.
- e. To facilitate visits and meetings between disciplines.
- f. To encourage MCM-aerosol developments.
- g. To assimilate the knowledge from past chamber experiments and make it more accessible to scientists.

Group 2: Long-range Transport of Pollutants

The group recommended the following.

- a. Existing data that could be used to examine LRT should be collected together to create relevant database. A workshop including participants from previous EU projects (*e.g.* TRADEOFF) and data centres as well as end users should be the first step to formulating a strategy to achieve this. T&TP or the ACCENT Data Task might then be able to provide the resources required.
- b. A workshop would be useful to identify measurement requirement (where, what, frequency of measurements). This could be linked to IGACO. ACCENT could provide support through the Infrastructure Task.
- c. A workshop to plan an Arctic experiment which would bring together experts in Arctic research and experts in LRT.
- d. Encourage interaction with the ACCENT Aerosols Activity, which can provide much advancement in the characterisation of aerosols, the ACCENT Modelling Task which could provide improvements in modelling techniques and the ACCENT Emissions Activity which should provide improved model inputs.

Group 3: Chemical weather

The group recommended the following.

- a. Organisation of a workshop or similar meeting with discussion groups on chemical weather. It would probably be wise to choose a subset of the issues discussed within the group to focus on at such a workshop, now that this group has take the task of defining the overall framework.
- b. Surveying the atmospheric sciences community to develop a listing of the currently operational (and standby) chemical weather forecast systems, subdivided into types (by scales and applications). A website with such a catalogue including links to the various operational systems would probably be of great service to the community.
- c. To link, *via* T&TP, with the chemistry-climate group to define metrics, as well as provide a mechanism for linking to the public in terms of understanding the relative value of different metrics (*e.g.* PM levels, visibility, *etc.*).

Group 4: Chemistry and Climate Interactions

The group recommended the following.

- a. A model experiment on **convection** (*David Stevenson*) to elucidate:
 - how changing climate will affect convection;
 - the impact of NO_x emissions from lightning
 - the impact of convection on chemistry?
- b. A workshop on the **nitrogen cycle** (*David Fowler*) (see Group 1)
- c. A model experiment on **natural variability**, studying. Perhaps the El Nino/ La Nina phenomena, or the North Atlantic Oscillation. There are possible links here to the RETRO project led by *Martin Schultz* and also to AMMA.
- d. To cooperate on **emissions** with the ACCENT- emissions/GEIA group led by *Claire Granier*.
- e. **Aerosols**: To cooperate in the completion of the AEROCOM exercise in 2005 in evaluating and reducing uncertainties in the aerosol direct climate effect. (*Hans Feichter and Frank Dentener*).
- f. To explore the area of **multiphase chemistry** with a view to it being an ACCENT topic since it appears to be of increasing interest. (*Maria Kanakidou*)
- g. **Metrics**: An effort should be made to define better and more representative metrics of climate change, air pollution and hydrological cycle perturbations that will also provide regional information. (*Ivar Isaksen and Frank Dentener*)

The T&TP steering group will review all these recommendations and decide with which to proceed. The recommendations will also be brought to the attention of the ACCENT community.

9. Individual Contributions from Principal Investigators

Chemical Complexity

David Fowler	The Causes of Non-linearities in Regional Atmospheric Mass Budgets for Oxidised and Reduced Nitrogen and Sulfur
M.E. Jenkin	Degradation of Volatile Organic Compounds: Some Areas of Uncertainty
Alastair C Lewis	Organic Compounds and Chemical Complexity
Michela Maione	Observation of Halogenated Hydrocarbons in the Troposphere
Paul S. Monks and Mark J. Jacob	Indications for the Importance of the Reactions of Ozone with Alkenes and the Concomitant Production of Peroxy Radicals

Long-range Transport

Isabelle Bey	Investigation of the Chemical State during Long Range Transport Events over the North Atlantic
H. Huntrieser	Ongoing Activities on Long-range Transport at DLR, Oberpfaffenhofen
Maarten Krol	Bridging the Gap between Global and Regional Scale Models
Paolo Laj	Evolution of Chemical and Physical Properties of Aerosol Particles during Transport: Implication for Cloud-forming Ability
Jose L. Palau, Millán M. Millán and Gorka Pérez-Landa	Contribution to Background Air Quality at Regional and Global Scales
Claire Reeves	Ozone Production in Polluted Air Masses undergoing Long-range Transport
Petra Seibert	Transport of atmospheric trace substances investigated with the FLEXPART and FLEXTRA models
P. James, H. Feldmann, H.-J. Kanter, H. E. Scheel, A. Stohl and T. Trickl	Atmospheric Long-range Transport and its Impact on the Trace-gas Distribution in the Free Troposphere over central Europe (ATMOFAST)
Vidmantas Ulevicius	Influence of Long-range Transport and Local Sources on Aerosol Formation and Growth in the Boundary Layer

Chemical Weather

Jørgen Brandt	THOR – an Integrated Air Pollution Forecasting and Scenario Management System
Hendrik Elbern	Data Assimilation for Chemical Weather Forecasting
Henk J. Eskes	Stratospheric Ozone Forecasts, Satellite Observations of the Tropospheric Composition and GMES
K.G. Ganev	Application of Functions influencing Air Pollution Problems
Mark G. Lawrence	Research Interests Overview
Stuart A. Penkett	Shipping as a source of NO _x at Weybourne

Chemistry and Climate

Russell Dickerson	Chemistry and Climate at the University of-Maryland
Johann Feichter	Development of Emission Strategies using an Advanced Aerosol Model
Millán M. Millán	The New Thinking relative to the Second Assessment Report
Christina Schnadt	Chemistry and Climate Studies at ETHZ

9.1 Chemical Complexity

The Causes of Non-linearities in Regional Atmospheric Mass Budgets for Oxidised and Reduced Nitrogen and Sulfur

A contribution to ACCENT T&TP: Chemical Complexity

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The Atmospheric Science Section at CEH Edinburgh has been analysing the trends in concentration and deposition of the major pollutants (all components of NO_x, NH_x and SO_x) in the UK for the period 1986-2004, for which high quantity monitoring networks have been in place.

The measured concentration and deposition fields show evidence of non-linearities in the spatial patterns of emission and deposition.

Sulfur compounds

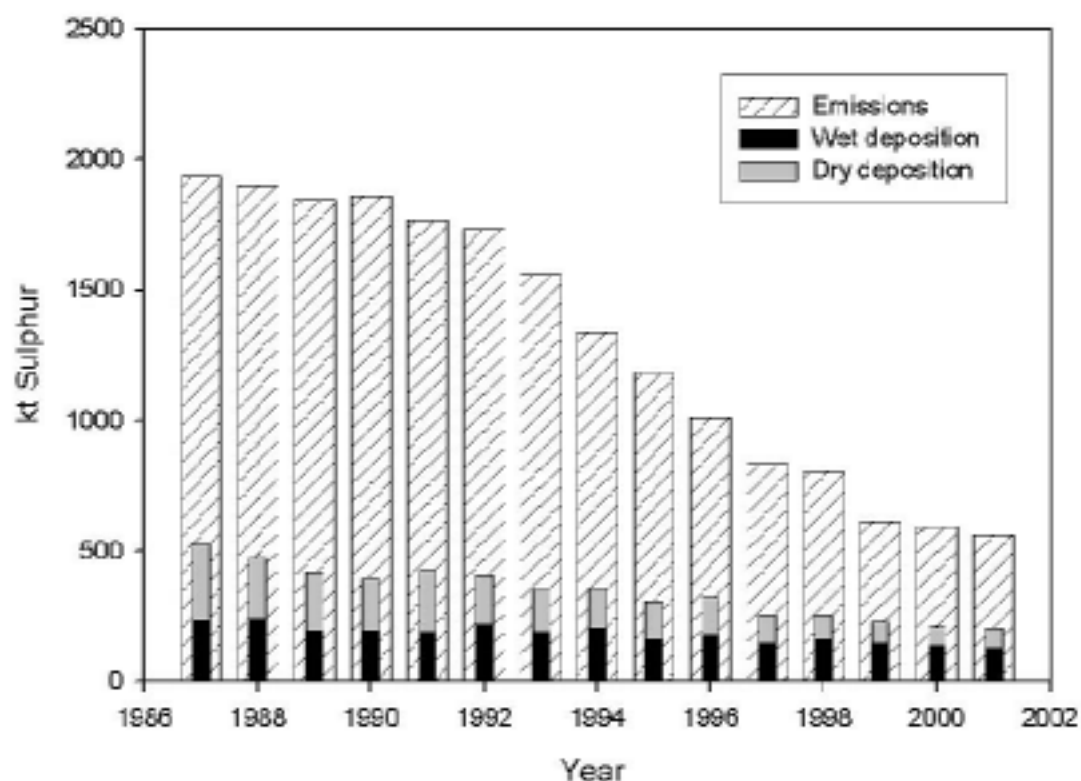


Figure 1. UK oxidised sulfur emission and deposition trends from 1987-2001

Considering country budgets, oxidised sulfur emissions have decreased by 71% from 1987-2001 while deposition has only declined by 61% (Figure 1). The partitioning of wet and dry deposition has also changed: the fraction of total sulfur deposition that is dry

deposited has declined from 55 to 40 % from 1987-2001. Over the same time period, the fraction of wet deposition has increased from 45 to 60 %.

The reduction in S deposition has not been spatially constant in the UK (Figure 2) and the greatest reductions are observed in the English Midlands.

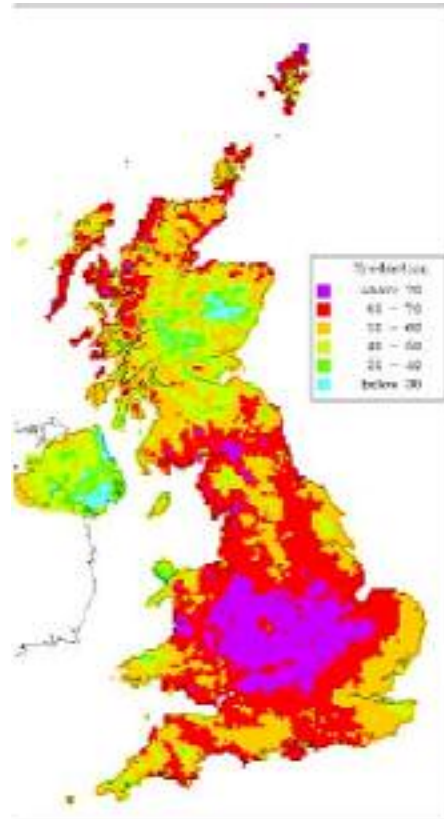


Figure 2. Relative reduction from 1987 to 2001 in the total deposition of non-marine sulfur (total deposition is the sum of dry, wet and cloud droplet deposition)

Reasons for the observed non-linearities in sulfur

1 Shipping

The effect of emissions from shipping on the sulfur deposition field is clear at west coast locations, where during a period in which land-based sulfur emissions declined by 50 %, no significant decline in concentrations of SO_4^{2-} in precipitation were observed. The sites affected are primarily the coastal regions of SW UK, where shipping sources contribute a substantial fraction of the deposited sulfur, but the effect is not detectable elsewhere.

2 Dry deposition: surface/canopy resistance (r_s) change with time

The surface resistance is regulated mainly by uptake in moisture on foliar surfaces, which, in turn, is strongly influenced by the presence of NH_3 . The large changes in emissions of SO_2 have changed the ratio of ambient SO_2/NH_3 and this influences the surface resistance over regional scales.

3 Changes in atmospheric processes

Points 1 & 2 have been examined while point 3 still needs to be addressed.

Nitrogen compounds

The concentrations and deposition of NO_3^- in precipitation have declined little following a reduction in emissions of 45% during the period 1987 to 2001.

Reasons for the observed non-linearities in nitrogen

1 Shipping

The shipping emissions may help explain the lack of trends in NO_3^- concentration in rain in the UK.

2 Atmospheric Processes

Point 2 is still to be addressed fully.

For reduced Nitrogen, minor changes in emissions have been made (reduction of ~10 %). However NH_4/SO_4 ratio changes have been observed (non-linear responses of the transformation and removal mechanisms).

CEH - Non-linearities work is in progress in collaboration with EMEP.

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Degradation of Volatile Organic Compounds: Some Areas of Uncertainty

A contribution to ACCENT T&TP: Chemical Complexity

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The processing of organic compounds in the atmosphere provides one of the best examples of chemical complexity related to the transport and transformation of pollutants. Volatile organic compounds (VOC) are emitted from both biogenic and anthropogenic sources, and emissions speciation data indicate that many hundreds of VOC are emitted. Each possesses different properties (*e.g.* reactivity; volatility) by virtue of structure and functional group content, and therefore has a different impact on the generation of secondary pollutants such as ozone and secondary organic aerosol (SOA). In the case of SOA formation, the mechanism of gas-to-particle transfer of semi-volatile and involatile products of VOC oxidation is not fully understood, and the likely important role of condensed phase reactions of organics in promoting gas-to-particle transfer has only recently been recognised.

The voxbox contributions described below aim to identify some existing areas of uncertainty in the understanding and impact of VOC oxidation. These are mainly based on experience gained through development and application of the Master Chemical Mechanism (MCM: Jenkin *et al.*, 1997; 2003; Saunders *et al.*, 2003), but should be regarded as examples, rather than an exhaustive list. Other areas of uncertainty, such as the degradation mechanisms for aromatic hydrocarbons, have been recognised for some years, and incremental improvements in understanding are being made. Particular uncertainties related to aromatic oxidation were presented by Mike Pilling in the Chemical Complexity discussions.

Oxidation of long-chain alkanes

Approximately 25 % of the emissions of anthropogenic non-methane VOC are in the form of $\geq C_5$ alkanes. This exceeds the contribution from C_2 - C_4 alkanes (*ca.* 20 %), aromatic hydrocarbons (*ca.* 20 %) and alkenes (*ca.* 8 %), all of which have been given significant attention. The MCM mechanisms for longer chain alkanes aim to represent the kinetic and mechanistic database, but rely heavily on parameters and pathways defined by analogy and with the use of structure-reactivity correlations. Recent testing of the MCM mechanisms for heptane and octane using the limited amount of chamber data available has suggested that the formation of ozone is significantly underestimated. Particular mechanistic uncertainties appear to relate to the further oxidation of bi- and multifunctional products generated in the early stages of the degradation. For example, major first generation products are believed to be γ -hydroxycarbonyls, but there is little experimental information on further oxidation of these species which might influence the radical budget, *e.g.* photolysis vs. OH reaction. In addition, it is possible that these products might isomerise to form cyclic hemi-acetals and highly reactive dihydrofuran products, following dehydration. It is therefore suggested that information is required in the following areas: (i) More chamber data on the photo-oxidation of long chain alkanes is needed, ideally including detection and quantification of bi- and multi-functional oxidised products; (ii) Kinetic and mechanistic data on the oxidation of relevant bi- and multi-functional oxidised products (*e.g.* hydroxycarbonyls) are required; and (iii) Detection methods for observing multifunctional products of VOC oxidation in the field need to be developed and/or applied.

Degradation of organic nitrates

Organic nitrates are sometimes referred to as minor products of VOC oxidation. In practice, a significant fraction of emitted organic material is converted to products containing nitrate groups. For example, even alkyl nitrates formed in the first oxidation step of emitted anthropogenic alkanes represent *ca.* 10 % of the first generation product yield of all emitted anthropogenic VOC. In addition, up to *ca.* 10 % of emitted isoprene and up to 25 % of emitted monoterpenes is converted into nitrate products, depending on the availability of NO_x. Various aspects of the atmospheric chemistry of organic nitrates are incompletely understood, even though their formation, transport and degradation potentially has an impact on the environment and climate in a number of ways, ranging from the inhibition of ozone formation on local/regional scales to influencing the global budget and distribution of NO_x and ozone. For example, there are no reported product studies of the OH initiated degradation of any organic nitrate, even though this is likely to be the major removal reaction in many cases. It is of particular importance to establish whether reaction with OH leads to release of NO_x, formation of more oxidised products which retain the nitrate group, or additional NO_x sequestration through formation of dinitrate products. In the latter two cases, it is possible that the sequential substitution of polar substituent groups can generate multifunctional products which more readily partition into the condensed phase, and therefore contribute to SOA.

Degradation of organic hydroperoxides

Hydroperoxides are also often considered as minor products of VOC oxidation. However, their formation through reactions of organic peroxy radicals with HO₂ is favoured at lower NO_x concentrations, and their formation from the global oxidation of biogenic hydrocarbons is likely to be considerable. Several recent appraisals of mechanisms of SOA formation have proposed that hydroperoxides play an important role. Not only are multifunctional hydroperoxides (*e.g.* as formed from monoterpenes) comparatively involatile, but their condensed phase association reactions with carbonyls to form involatile peroxyhemiacetals are believed to make an important contribution to SOA formation. The appraisals have included laboratory studies (Tobias and Ziemann, 2000), simulations of chamber SOA yields using detailed mechanisms (Jenkin, 2004; Johnson *et al.*, 2004) and global modelling studies (Bonn *et al.*, 2004). Despite this potential importance, hydroperoxides have not been well studied in the laboratory (partially due to their explosive character, no doubt). There is only limited information on their photolysis, and the kinetics of the OH reaction has only been studied for CH₃OOH. Clearly, additional data for other hydroperoxides is required to allow structure-reactivity relationships to be developed. More information is required on multifunctional products containing hydroperoxy groups, and their role in SOA formation. Field data on multifunctional hydroperoxides in the gaseous and condensed phases are also required.

Short-lived emitted VOC

Some emitted hydrocarbons are exceptionally reactive, such that they are suppressed to very low concentrations in short distance and time scales from the emission point. It is therefore possible that their contribution to emissions can be underestimated or overlooked. Well known examples are certain types of monoterpene and sesquiterpene, which react very rapidly with ozone. For instance, the monoterpenes α -phellandrene and α -terpinene have lifetimes of only 7 minutes and 2 minutes with respect to reaction with 30 ppb ozone, and are not expected to survive transport from the forest canopy. Both these monoterpenes are alkyl substituted cyclohexa-1,3-dienes. Similar diene species are known to be emitted in vehicle exhaust, and have also been shown react rapidly with NO₂. It is likely that their

contribution to emitted VOC speciation is underestimated, because they react away in exhaust samples in the presence of high NO_x. For example, cyclohexa-1,3-diene has a lifetime of ca. 7 minutes in an exhaust sample containing 50 ppm NO₂, and ca. 2 days in a polluted urban air sample containing 100 ppb NO₂. Similarly, they are rarely detected in the atmosphere owing to their reactivity with NO₂ and O₃. The NO₂-initiated oxidation of cyclohexa-1,3-diene has recently been shown to form HO_x radicals in ca. 80 % yield. Cyclohexa-1,3-diene has a lifetime of ca. 20 minutes with respect to reaction with 30 ppb ozone, and alkyl substituted analogues are likely to be significantly shorter lived. These reactions may be free radical sources at the low concentrations of ozone typical of polluted urban locations.

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Organic Compounds and Chemical Complexity

A contribution to ACCENT-T&TP: Chemical Complexity

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Organic compounds play a central role in many atmospheric processes including both the gas phase chemistry controlling tropospheric ozone and condensed phase processes generating organic aerosol. Although studied in much detail over many decades, advances in understanding have generally been achieved concurrently with advances in the capabilities of observational techniques. It is interesting therefore to consider how our view of organic species in the atmosphere changes as our ability to measure new species and in new location evolves over time. The most important improvements in observational methods have not simply resulted in detecting lower concentrations, but in allowing detection of new functional groups and classes of species. The ubiquitous nature of species such as methanol and acetone is now well understood, yet a review of literature only 10 - 15 years old shows almost no mention of their presence. Viewed from the crudest measure of importance, that of mass of carbon, it is highly surprising that these species could have evaded detection. Techniques such as PTR-MS have allowed detection of small functionalised species at a much higher time resolution than possible previously, and in parallel developments in speciation of higher molecular weight organic compounds with ultra high analytical resolution techniques such as GCxGC have occurred. A result is that methods now exist which allow organic measurements as fast as 1 Hz frequency or which yield detail on many thousands of individual organic compounds in a single analysis procedure. Observational techniques have perhaps therefore outstripped interpretive methods and this raises important questions about both the *use* and *usefulness* of such data.

In the past from a field measurement perspective, there has been a consensus that when trying to understand the atmosphere through a combination of observations and models, that the more measurements that are made the better. However we approach a situation where speciated organic measurements exceed our ability to assimilate such data into any model (be it number of species or frequency of observation), and how we deal with this is perhaps at the centre of many aspects of what is referred to often as 'chemical complexity'. A key aspect of using such data is therefore likely to be in determining the correct degree of observational complexity required to describe most if not all of the processes occurring within a region of the atmosphere. A difficulty will naturally be that with the exception of perhaps the most remote parts of the atmosphere, this complexity will be dynamically changing with emission source, mixing and transport processes and degree of oxidation.

An interesting example of how the degree of organic complexity changes as a function of air-mass type and meteorological transport can be seen at remote monitoring sites. From observations at Mace Head in Ireland under Westerly conditions when airflow arrives from the oceanic sector, a surprisingly small set of organic compounds are needed to describe, at least from a radical source and sink perspective, the *in-situ* chemistry. These number a handful of small oxygenated molecules (acetone, acetaldehyde, methanol), and the longer lived aliphatic species (*e.g.* ethane, propane, acetylene). Deploying extremely high resolution techniques at this location, yields observations which show that a highly complex mixture is still present in air (many hundreds of hydrocarbon like species), yet the influence on for example ozone processes is negligible due to a combination of low concentrations and low relative reactivity. In this case the transport period of around 4

days over Atlantic still leaves a complex mixture, but one of low reactivity compared to close to emission. At the same location, air-masses from an Easterly direction, influenced strongly by terrestrial sources, have somewhat increased complexity (measured purely as the absolute number of species that can be detected), but orders of magnitude greater reactivity. In this second case description of the *in-situ* chemistry naturally requires much greater model complexity and in the inclusion of many more organic species. Complexity is not therefore defined purely by the *number* of species present but is much more complex combination of speciation, functionality and reactivity.

For a given set of atmospheric conditions it is generally possible to tailor chemical models to fit the degree of complexity needed to describe some local or regionally averaged observation. Typically this is done on the idealised case study days, - but what should be the approach in an environment when this is dynamically changing? Most observational experiments (especially those from aircraft) probe the transitions between regimes rather than the chemical evolution of a single system. A reduced or simplified model optimised for one environment may not be optimal for the next system to be encountered. Determining the lowest degree of organic complexity needed to describe the atmosphere at a point in time, requires however *a priori* knowledge of speciation and variability. Whether this must be determined experimentally or can be estimated from previous encounters of similar air-mass types is likely to vary from case to case. High time resolution observations of some organic species (for example toluene, propene *etc.*) from anthropogenic sources, may follow so closely the behaviour of CO that the latter could be used as a time resolved proxy. In such cases the added complexity of collecting and utilising 1 Hz organic data may be questionable. In other environments, where no simple proxy exists or where flux determination is the objective (for example isoprene in the atmosphere), high time resolution observations add significant information.

In terms of complexity of the observed organic mixture, this may also be something that can be estimated with a degree of confidence without always requiring resolution of thousands of species in air. Whilst the highest resolution techniques may isolate for example several hundred monoaromatic species, no model can utilise this data, and in many cases no kinetic data exists. At best therefore the speciated data on such a class may be recombined into a generic species which propagates the properties of these species for example in terms of ozone production or aerosol yield.

In urban environments much of complexity is contributed to by petrochemical and related sources. That is not to say that the chemistry is necessarily dominated by this source, but purely in terms of compound numbers it is most significant, a natural consequence of exponentially increasing isomeric forms possible with the gasoline and diesel fuel ranges. For a given location it may be desirable therefore to produce a simplified subset but one which carries with it relevant chemical properties such as functionality and molecular weight, which represents the correct quantities of carbon and reactivity, but which can be incorporated efficiently within any model. Since fuel composition varies by geographic location, source and time of year, a universal scaling factor is unlikely to be applicable, but the approach is more tractable than attempting to utilise complex chemical observations. The appropriate place therefore for high resolution speciated observations may be in setting the correct reactivity and functionality for a given location or chemical climate, cross referenced with for example observations of radical lifetimes. Similarly high time resolution measurements may be needed to determine initially which species can be represented in terms of variability by simpler proxies, whilst focussing more on those for which no proxy exist.

Observation of Halogenated Hydrocarbons in the Troposphere

A contribution to ACCENT-T&TP: Chemical Complexity

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27 halogenated hydrocarbons (see Appendix) are continuously monitored at the mountain station (2165 m asl) of Mt Cimone (Northern Apennines, Italy) since 2001. They include chlorofluorocarbons (CFCs), halons, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), halogenated solvents, and methyl halides. All of them, except the methyl halides, are of anthropogenic origin.

The halogenated halocarbons play a major role in several atmospheric phenomena. Meanwhile the most stable are stratospheric ozone depleting substances and radiatively active gases strongly contributing to global warming, the most reactive ones induce perturbations to the oxidative capacity of the troposphere; and seems to contribute to new particle production in coastal regions. These compounds are monitored on a global scale in the AGAGE (Advanced Global Atmospheric Gas Experiment) stations and, on a European scale in the SOGE (System of Observation for Halogenated Greenhouse Gases in Europe) stations. The two networks are closely linked through the use of the same calibration scale. Most of the AGAGE and SOGE stations are located in remote or semi-remote sites and are therefore representative of a baseline situation. Mt Cimone, together with the Jungfraujoch (Bernaise Alps, Switzerland) station is better positioned to observe emissions from sources.

The study is supported by EC through two different projects funded in FP5 and FP6 (SOGE and SOGE-A, respectively) consisting in a combination of measurements and models aimed at assessing long term trends and at identifying source strength on a European regional base.

Methodology

GC-MS measurements

The halogenated hydrocarbons are semi-continuously (6 samples/day) monitored by capillary gas chromatography-quadrupole mass spectrometry preceded by on-line sampling/adsorption.

Quality assurance

In order to obtain air quality data, each actual air sample chromatographic run is “bracketed” with two calibration run using real-air “working secondary standards” currently linked to two absolute calibration scales for halocarbons which reside at the Scripps Institution of Oceanography (SIO98 scale-SIO, La Jolla, Ca, USA) and at Bristol University (UB98 scale, University of Bristol, Bristol, UK). This procedure also allows us to correct for the instrumental drift in the signal response of the mass spectrometer that normally decrease during working time. To ensure quantitative detection one target and one or two qualifier ions are monitored using custom software developed at SIO. Furthermore, this specialised software enables constant monitoring of ion ratios, peak width ratios, and a range of other analytical parameters as a diagnostic tool of overall instrumental performance.

Data analysis

The statistical analysis of concentration data is based on air masses back trajectories. Backward trajectories were computed by *MeteoSwiss* twice a day and go back 48h. In order to identify potential source regions of pollutants, these trajectories were combined with measured concentration data. The accumulated residence times of the trajectories in grid cells were calculated and transport of air masses to the measurement site were revealed by contour plots.

Baseline concentrations were calculated using the AGAGE filtering procedure. However, results should be considered as preliminary since at the moment they were analysed the available data set was just sufficient for this kind of evaluation. A larger database is now available and it is currently being processed. More reliable results are expected soon.

Some selected results

Some examples of analysis performed on the measured concentration data are reported below.

In Figure 1 are represented potential source regions for the partly anthropogenic partly biogenic CH_3Br . Units indicates averaged concentrations above the baseline linked to trajectories that were in the boundary layer when they passed over the respective grid cell. The patterns is likely to be the result of a combination of natural emissions from the Mediterranean area but also anthropogenic in correspondence with the transports of an anthropogenic tracer, HFC-125 (see Figure 2). Moreover a relevant emission is related to some activity (maybe agricultural) in central Italy.

Figure 1

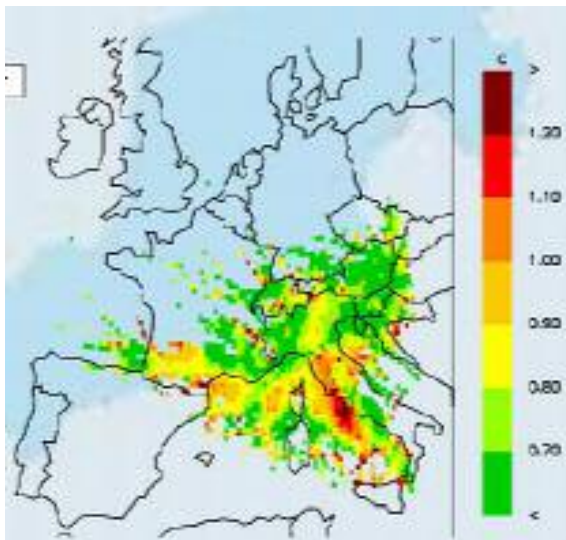
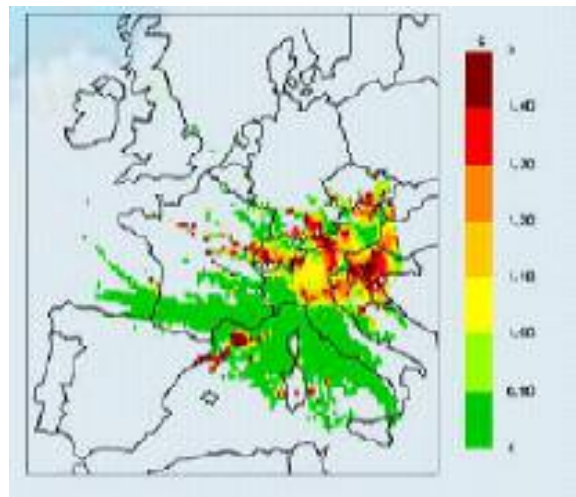


Figure 2



In Figures 3 and 4 some trends are shown. The red line represent the final smooth curve line and the green one the long-term trend curve. The first derivative of the long-term trend curve is used to give the instantaneous growth rate (in pptv and in %) shown in the plots below. Increase of the CFC replacement HFC-125 is evident together with the seasonal trend related to OH reactivity (Figure 3). Decrease of CH_3CCl_3 and seasonal trend are reported in Figure 4.

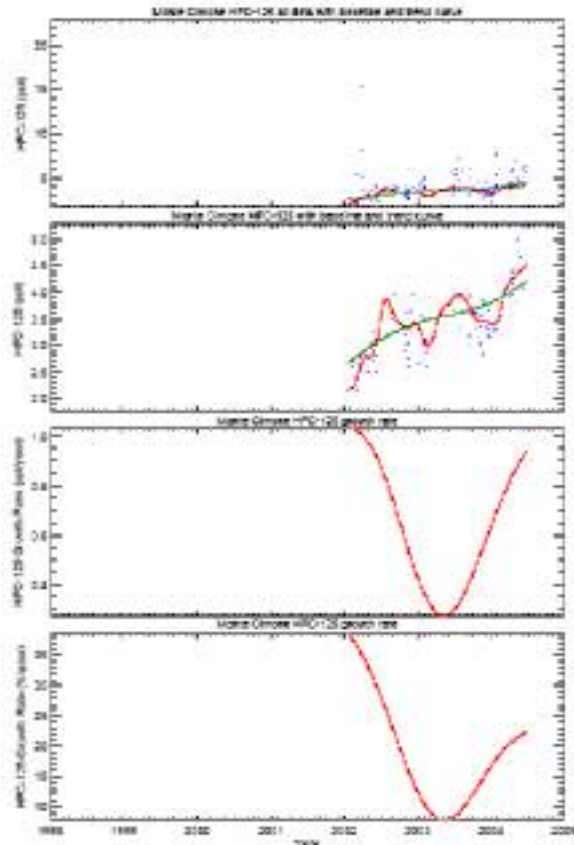


Figure 3

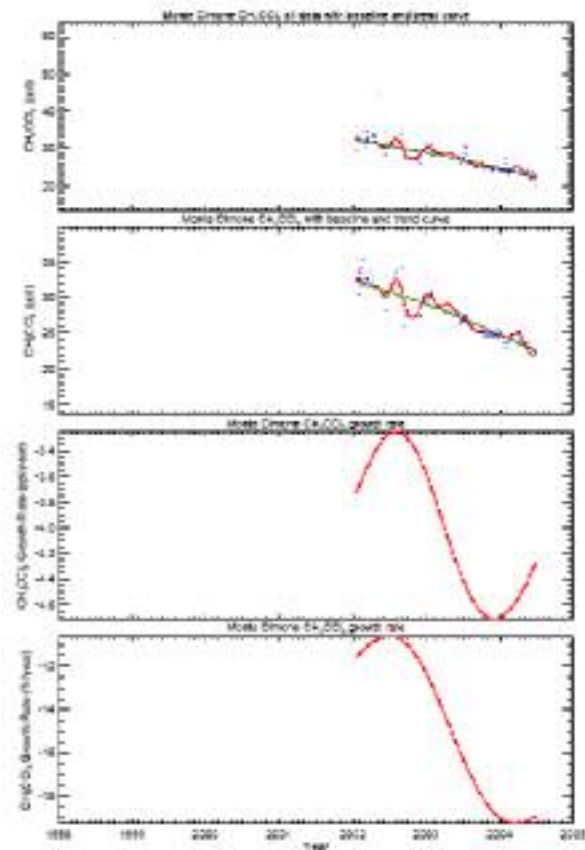


Figure 4

Appendix: List of the compounds monitored

C ₂ F ₆	HFC-23	SF ₆	Halon 1301	CFC-115
HFC-125	HFC-143a	CFC-12	HCFC-22	CH ₃ Cl
HFC-134a	Halon 1211	HFC-152b	CFC-114	CH ₃ Br
HCFC-142b	HCFC-124b	CFC-11	CH ₃ I	CH ₂ Cl ₂
HCFC-141b	CFC-113	CHCl ₃	CCl ₄	CHCl ₃
CH ₃ CCl ₃	C ₂ Cl ₄			

Indications for the Importance of the Reactions of Ozone with Alkenes and the Concomitant Production of Peroxy Radicals

A contribution to ACCENT-T&TP: Chemical Complexity

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One route of growing importance with respect to the production of peroxy radicals, particularly in the boundary layer, is production of HO_x from the reactions between ozone and alkenes. The ozonolysis of alkenes can lead to the direct production of the OH radical at varying yields (between 7-100 %) depending on the structure of the alkene, and is normally accompanied by the co-production of an (organic) peroxy radical. As compared to both the reactions of OH and NO₃ with alkenes the initial rate of the reaction of ozone with an alkene is relatively slow; this can be offset under regimes where there are high concentrations of alkenes and/or ozone. Peroxy radicals are key intermediates and chain carriers in the gas phase oxidation of volatile organic compounds, and owing to their short lifetime their fate is indicative of the photochemical production or destruction of ozone.

For example, work from this group (Salisbury *et al.*, 2001) has shown that at night in semi-polluted conditions the reaction between ozone and alkenes can be a more significant loss process for alkenes than the concomitant reactions with NO₃. Indeed, the reaction of ozone with alkenes was the dominant source of peroxy radicals at night.

More recently a series of measurements were made at Writtle College, Writtle, Essex (51° 44'12''N; 0° 25' 28''E), a site approximately 25 miles northeast of central London during the summer of 2003. The highest ever recorded daytime air temperature in the United Kingdom occurred in southeast England during August 2003, and was accompanied by periods of high ozone and poor air quality. Back trajectories calculated during the 'heat-wave' period, show the air having been stagnant over the UK or northern Europe for at least 5 days prior to arriving at the measurement site. Ozone was observed to exceed 100ppbv on five occasions from 6th – 10th August 2003 reaching a maximum value of 156 ppbv on 10th August, the highest levels observed in the U.K. since 1981 (see Figure 1). Maximum daily concentrations of peroxy radicals were observed to be > 100 pptv during this heat-wave period, with the maxima occurring several hours after solar noon (see Figure 1).

The strong asymmetric nature of the diurnal cycle with respect to primary production by photolysis is indicative of the role of non-photolytic sources of HO_x. The data in Figure 2 is suggestive of the role of the reaction between ozone and biogenics, in particular isoprene, in the production of peroxy radicals. There is a significant "chicken and egg" question in relation to the production of the large concentrations of ozone in the sense of efficiency of the production of the ozone in relation to production of peroxy radicals from the isoprene-ozone reaction. The question arises, how significant is this compared to other radical sources? Of the fifteen alkenes measured at TORCH, isoprene is by far the biggest contributor to radical production in the afternoon (see Figure 2).

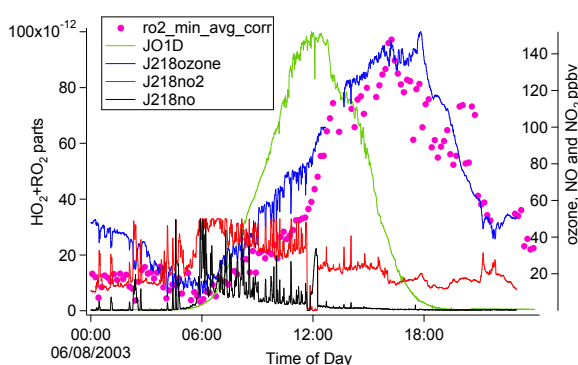


Figure 1. Peroxy radical and trace gas concentrations from 6th August 2003 during the summer heat-wave.

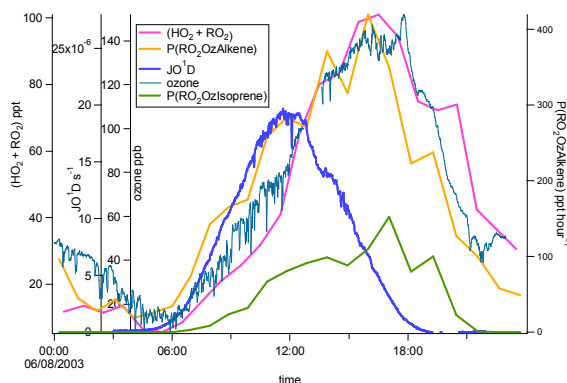


Figure 2. Calculated RO₂ production rates from the reactions between ozone and alkenes.

The strong asymmetric nature of the diurnal cycle with respect to primary production by photolysis is indicative of the role of non-photolytic sources of HO_x. The data in Figure 2 is suggestive of the role of the reaction between ozone and biogenics, in particular isoprene, in the production of peroxy radicals. There is a significant “chicken and egg” question in relation to the production of the large concentrations of ozone in the sense of efficiency of the production of the ozone in relation to production of peroxy radicals from the isoprene-ozone reaction. The question arises, how significant is this compared to other radical sources? Of the fifteen alkenes measured at TORCH, isoprene is by far the biggest contributor to radical production in the afternoon (see Figure 2).

The results begin to point to the importance of ozone-alkene chemistry, long known to exist, in the production of oxidants on a regional scale. The link between biogenic compounds and ozone-alkene chemistry presents interesting questions in relationship to future scenarios for regional air quality in terms of chemistry-climate interactions.

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9.2 Long-range Transport

Investigation of the Chemical State during Long Range Transport Events over the North Atlantic

A contribution to ACCENT-T&TP: Long-range Transport

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We are currently investigating the long range transport (LRT) of ozone-related pollution over the North Atlantic. We especially focus on quantifying to what extent the LRT events contribute to a perturbation of the chemical states over that region. For that purpose we use a global chemical transport model (the GEOS-CHEM model [Bey *et al.*, 2001]) as well as the aircraft observations taken during the ACSOE (Atmospheric Chemistry Studies in an Oceanic Environment) experiment.

The ACSOE campaign was dedicated to the survey of the atmospheric composition over the Atlantic Ocean between the North American and European continents with a special focus on quantifying the impact of pollution [Reeves *et al.*, 2002; Penkett *et al.*, 2004]. The UK Meteorological Office C-130 aircraft performed several research flights around the Azores in April and September 1997 and captured several transatlantic transport events. During one of these flights, the aircraft flew south of the Azores through hurricane Erica's outflow and back trajectories indicated that some polluted air masses found close to the hurricane were uplifted by a frontal system over North America 5 to 6 days earlier [Penkett *et al.*, 2004]. Figure 1 shows an example of comparison between the model results and the observations for this flight. The model reproduces the variation of ozone quite well ($r^2=0.75$) but underestimates it by about 10 ppbv. We find that the simulated hemispherical ozone contribution¹ remains constant at a given altitude during the flight, while the North American contribution² increases up to 20 ppbv at 6km of altitude from 16 UTC onward, consistently with the backtrajectory analysis. In agreement with the observations, simulated CO and NO_y concentrations are also enhanced during the same period (not shown). We find that this enhancement is due to North American anthropogenic emissions. In this case, NO_y is mostly composed of PANs.

We further characterize the impact of LRT events using production and loss rates obtained in April 1997 from observationally constrained chemical point model calculations [Reeves *et al.*, 2002]. The observed daytime chemical production terms are compared with those obtained in our model in Figure 2. The chemical terms are simulated correctly in general. However, the ozone production (P_{O_3}) is overestimated in the lower troposphere, and especially in the marine boundary layer. This might be due to the strong dependency of P_{O_3}

¹ The hemispherical contribution includes the stratospheric input and the ozone produced through the oxidation of biogenic emissions of precursors and methane. This contribution is diagnosed with a simulation in which all anthropogenic emissions are turned off.

² The North American contribution corresponds to the fraction of ozone due to ozone precursors of North American origins. This contribution is diagnosed by subtracting the results of a standard simulation (i.e. with all emissions turned on) from those obtained from a simulation in which North American emissions are turned off.

on NO_x concentrations, which may be too high in the model because of the smearing of NO_x emissions from ships in the coarse grid boxes. Figure 2b also shows the results of a sensitivity simulation in which ship emissions have been turned off. Although results improve, P_{O_3} (and thus the net P_{O_3}) is still overestimated in the marine boundary layer.

The activities to be included in AT2 will further investigate the perturbation of the chemical terms by LRT events by using additional observations obtained during various aircraft campaign such as ACTO, EXPORT and ITOP.

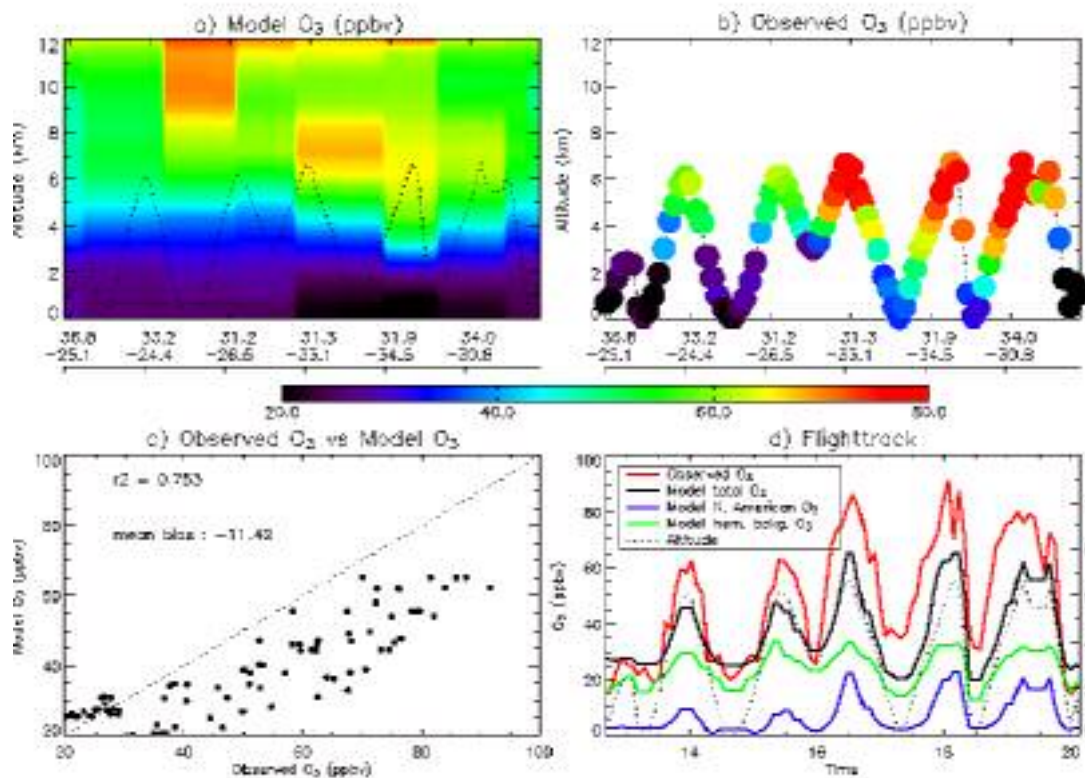


Figure 1: Model (a) and measured (b) O_3 (ppbv) along the flight track of the C-130 British Aircraft on 14th Sept. during the ACSOE (Atmospheric Chemistry Studies in the Oceanic Environment) campaign, over the North Atlantic. (c) Correlation between observed and model O_3 . (d) Time series along the flight track of observed ozone (red), model total O_3 (black), hemispheric background O_3 (green), and North American O_3 (blue).

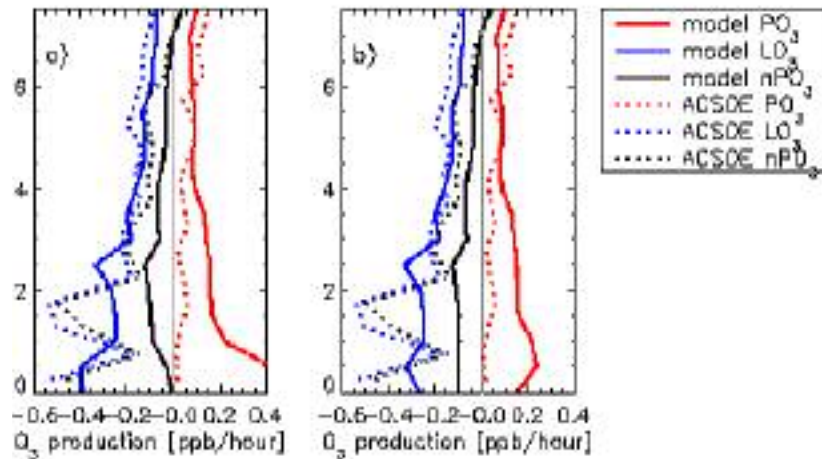


Figure 2: O₃ production (red), O₃ destruction (blue), and O₃ net production (black), over the North Atlantic for the ACSOE April flights. Dotted line (a and b): data from Reeves *et al.* [2002]. Continuous line: (a) standard simulation and (b) simulation without ship emissions.

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Ongoing Activities on Long-range Transport at DLR, Oberpfaffenhofen

A contribution to ACCENT-T&TP: Long-range Transport

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The DLR-Oberpfaffenhofen (H. Huntrieser and H. Schlager) has recently contributed to one of the review chapters in the new book on long-range transport (LRT) by A. Stohl (*Springer Verlag, 2004*): "Air Pollution Export From and Import to Europe: Experimental Evidence" [*Huntrieser and Schlager, 2004*].

In our "voxboxes" results from the German CONTRACE project were presented. The CONTRACE project investigated the uplift of pollution in frontal systems (warm conveyor belts) over North America and the transport of these air masses to Europe. Two airborne field experiments were carried out from southern Germany in fall 2001 and summer 2003. The DLR research aircraft Falcon was equipped with a complex instrumentation to measure NO, NO_y, CO, CO₂, O₃, J(NO₂), acetone, SO₂, ions, H₂O₂, formaldehyde, NMHC, J(O¹D) and particles. An extensive set of chemical and meteorological forecast products, including trajectory calculations, was developed and used in combination with satellite images to plan the flights. A passive tracer for surface emissions (CO) was included in the forecast models (FLEXPART and MATCH-MPIC) to separate the regional and intercontinental transport of polluted air masses.

During the airborne CONTRACE field experiment carried out in November 2001 a number of polluted layers of North American (NA) origin were observed in the free troposphere over Europe. For the first time forecasts from a Lagrangian particle dispersion model were used to predict the NA pollution events and to direct a research aircraft very precisely into these polluted layers above Europe [Lawrence *et al.*, 2003; Stohl *et al.*, 2003a-b; Huntrieser *et al.*, 2004]. Two of the NA pollution events were presented - one in detail (case November 19th) and a second more briefly (case November 22nd). An exceptional result was that the first pollution plume could be traced with the model and trace gas measurements (airborne and surface) for a period of one week, from the source region over the eastern U.S. to its decay over the Alps. On November 14-15th a warm conveyor belt lifted the leading edge of the pollution plume over the eastern U.S. to the mid troposphere where it remained during the transport over the Atlantic. On November 19th the plume was intersected with the research aircraft over Scandinavia at an altitude between 2 and 4 km. Elevated CO (170), O₃ (53), NO_y (1.1), acetone (5.0), and SO₂ (2.6) mixing ratios (nmol mol⁻¹) were measured. A positive O₃-CO correlation was observed in the plume. The observations indicate that the enhanced levels of ozone were already produced near the source region over the eastern U.S. and not during the transit. In the next days one branch of the plume then turned to the south and descended to ground level over the Alpine region. Elevated O₃ (54 nmol mol⁻¹) and CO (168 nmol mol⁻¹) were observed at the mountain site Zugspitze (southern Germany) during two days. At the Arosa Alpine site in Switzerland the highest daily ozone means of November 2001 were observed during this pollution event from North America.

Planned activities at DLR, Oberpfaffenhofen

Future DLR plans were presented where the project IMPACT was mentioned. In spring and autumn 2005, and spring 2006 three field experiments are planned to be carried out at Schneefernerhaus (2650 m, close to Zugspitze) to investigate the LRT from North America (NA) and Asia, and to study its impact on the Alpine region. Instruments for the measurement of formaldehyde (photochemical activity), acetonitrile (forest fires), NO_y and SO₂ (industrial emissions) will be provided by DLR and MPI-K. Further IMPACT tools and measurements that will be used are (support by ACCENT?):

- FLEXTRA/FLEXPART trajectory and tracer model (A. Stohl, NILU)
- GAW-Stations (UFS and Hohenpeissenberg)
- H₂O- and O₃-lidar (UFS and IMK-IFU Garmisch)
- Satellite data (SCIA and MSG)
- Aircraft measurements (DLR Falcon and CARIBIC)
- Alpine sites (Sonnblick, Jungfraujoch, Davos, Arosa and Mt. Cimone)

The objectives of the IMPACT project are to study:

- ozone (+precursor) increase in NA plumes
- horizontal and vertical extension of NA plumes
- frequency of NA plumes over Europe

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Bridging the Gap between Global and Regional Scale Models

A contribution to ACCENT-T&TP: Long-range Transport

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Research questions addressed and their relevance for T&TP

What is the budget over Europe of Aerosols and photochemical species like ozone and NO_y?

What are the model uncertainties associated with resolution, treatment of wet and dry removal of species, etc.?

Can we estimate sources of compounds from measurements?

The tool that has been developed to address these issues is the two-way nested chemistry transport model TM5. Locally the resolution can be refined to a horizontal resolution of 1×1 degree in order to allow a useful comparison with measurements made at the surface, from aircraft or by satellites. Boundary conditions are provided by a global simulation with the same chemistry and transport parameters, but at a lower resolution. Zoom regions can be added in a flexible way. Currently, zoom regions have been defined over Europe, North America and over Asia. In this way, the TM5 model tries to bridge the gap that exists between the regional scale models and the global models. While regional models consider local air quality, with TM5 global issues like long range transport can also be addressed.

The model is introduced in a ACP(D) paper (*Atmos. Chem. Phys. Discuss.*, **4**, 3975-4018, 2004). Here the advantage of higher resolution in comparisons with station data is addressed. Also a study with artificial tracers is presented in which the effects of resolution on the transport of an ozone-like tracer is shown.

Currently, the model is operating with the lumped CBM4 chemistry. We are currently implementing aerosols in order to study the aerosol budget over Europe within the PHOENICS project. TM5 also joins the AEROCOM intercomparison exercise as well as the EuroDelta project.

The adjoint TM5 model, only taking into account the linear transport of chemicals, has been developed. With the adjoint model, source-receptor relations can be calculated which quantify the sensitivity of a measurement for emissions upwind of the measurement location. These relationships are very successful in the analysis of measurement data from field campaigns. Furthermore, these relationships can be used to estimate the sources of a measured compound. This approach was shown to work for the methane emissions using measurements over Europe. Using inverse modelling techniques, Peter Bergamaschi (ACPD, to appear) showed that the methane emission estimates from France and Germany are probably too low, while the natural wetland emissions from Finland are probably overestimated by the bottom-up emission inventories.

Attending the Long-range Transport discussion group I was a bit surprised about the large gap that still exists between researchers that try to model the atmosphere and those who try to sample it. I think that ACCENT should play an important role in closing this gap by stimulating the exchange of ideas between the two research communities. As addressed in the meeting, measurements are very valuable for modelers. But, in my opinion, experimentalists should more often consult models (or modelers) in order to have their hypothesis tested.

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Evolution of Chemical and Physical Properties of Aerosol Particles during Transport: Implication for Cloud-forming Ability

A contribution to ACCENT-T&TP: Long-range Transport

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There are strong evidences for long-range transport (LRT) of particles, at the European scale but also intercontinental. Polluted layers observed during airborne campaigns over the Atlantic and Pacific Oceans contain large concentration of particles in the accumulation mode (50-500 nm). LRT can regulate particle mass far from emission sources, as a result of both transport of gaseous precursors and submicron particles. However, to which extent LRT regulates particle number concentration far from emission sources and in the free troposphere is still largely unknown. There are a number of reasons for this uncertainty in determining the spatial variability and the origin of atmospheric particulate material. The lack of coordinated measurements of particle properties at the European scale is one of them.

At present, available particle properties at remote field sites mostly concern the mass of the particle (PM₁₀ and PM_{2.5}). It is clear that, due to the complex nature of the particles, this information is not sufficient for air quality studies. In fact, present-day models failed to accurately describe observed spatial and temporal variations of aerosols over Europe. A knowledge of additional parameters measured on a routine basis at selected field sites along major transport corridors would be extremely useful to improve and provide constraints to modelling.

Size distribution of particles is one of the key parameters to be monitored. There is evidence that the air mass typology is not sufficient to characterize a particular aerosol size distribution. This means that assuming typical distribution (*i.e.* Jaenicke size distribution) for a given air-mass can be misleading. The size distribution is not a conservative parameter during transport due to sources and sinks taking place during transport, in particular over the continents. It implies that knowing the size evolution of a particle population provides strong constraints on sources and sinks.

Sources of aerosol particles are clear not well described. In particular, the particle nucleation rate in the atmosphere is still an opened question. There are new evidences that primary and secondary nucleation can take place in various type of environments including coastal zones, boreal forests and even urban areas. This is a great limitation for quantifying LRT. Monitoring the nanoparticle fraction (< 10nm) at selected sites, in addition to more process oriented studies, would contribute to better quantification of the homogeneous nucleation source in different environments.

The multiplicity of particle sources and of the physical and chemical forcing acting on a particle population (*i.e.* oxidation of primary aerosols, deposition of gases, physical processes such as coagulation are very effective to modify the original aerosol population) lead to particle complexity that is not fully resolved by current analytical techniques in particular for the organic fraction. A complete speciation of the organic fraction cannot be organized on a monitoring level given the complexity and the financial and human cost

involved for the use of advanced analytical tools. LRT studies can certainly benefit from determination of selected tracers as for Levoglucosan for biomass combustion, but, this is not organized on a large scale so far. The use of aerosol volatility measurements (size distribution at different temperature) as a proxy for particle complexity and ageing could offer a simpler approach for monitoring purposes once the relationship between volatility and chemical complexity is better understood.

The graph in Figure 1 shows how the hygroscopic character of the particles increases with increasing volatility temperature. The hygroscopic character corresponds, in that case, to a processed, thus more oxidized, aerosol population. One important consequence of the chemical and physical evolution of the aerosol properties during LRT transport is to increase the degree of mixing. The mixing properties of the aerosol and consequently its surface properties are important to predict both optical and hygroscopic properties and therefore quantifying climatic impact or wet deposition.

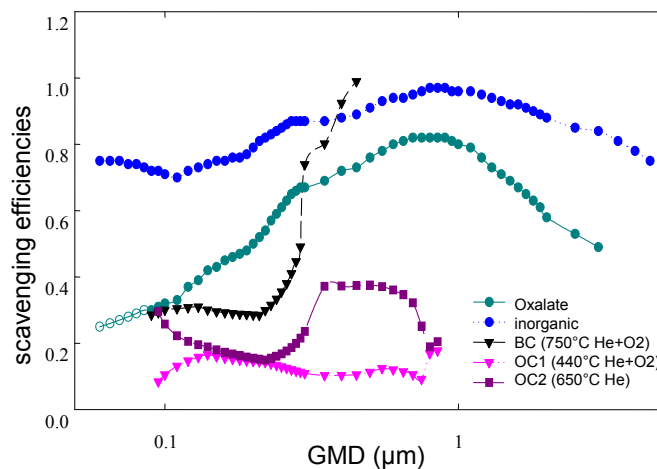


Figure 1: Scavenging efficiency of aerosol particles as a function of size and composition. Note that the efficiency increases with volatility temperature (OC1, OC2 and BC)

A fraction of the aerosol is internally mixed far from sources but techniques that can derive the mixing parameter (TDMA) are still of limited access over Europe. The chemical state of the aerosol surface is certainly an important parameter that control both hygroscopicity and reactivity of the particle. This is a primary parameter affected by transport in the atmosphere as a result of condensation of gases (from both biogenic and anthropogenic activities).

As an example, the following graph (Figure 2) illustrates how the scavenged fraction of particles in cloud is lower for maritime air masses than for continental air masses. The limited number of activated particles in maritime air masses is most likely a result of the presence of hydrophobic organic compounds deposited during transport inland. The evolution of the surface state of the particle is a primary parameter controlling impact of aerosols on atmospheric processes relevant to LRT

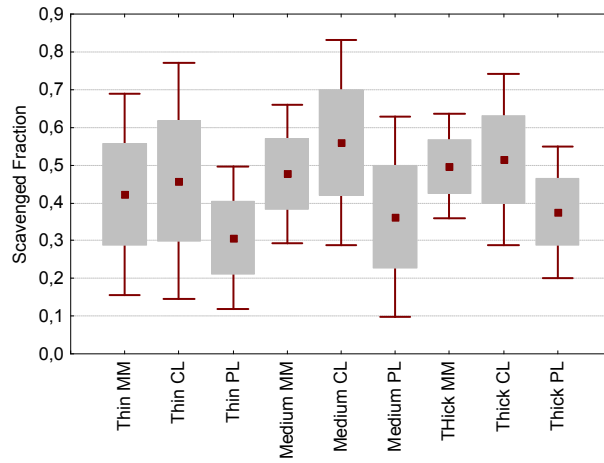


Figure 2: Statistical analysis of the CCN fraction for the 9 classes of samples showing mean of the population, 1 standard deviation (box) and 1.96 standard deviation (whiskers), respectively. Modified Maritime (1), Continental (2) and Polluted (3) and thin (A), medium-thin (B), medium-thick (C) and thick (D) clouds.

Contribution to Background Air Quality at Regional and Global Scales

A contribution to ACCENT-T&TP: Long-range Transport

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The transport of air pollutants (mainly tracers and SO₂ plumes) in stratified layers over land was documented in the US in the mid-to-late 1960s (Singer and Smith, 1966). Some of the available results were consolidated in the reports by Slade (1968) and ASME (1973) and reviewed by Pooler and Niemeyer (1971). For industrial stacks, the formation of stable plumes was considered a rare phenomenon resulting from the emission of hot effluents into a stable atmosphere (for a thin but wide, "fanning-type" plume), and with no shear (for a thin and narrow, "ribbon-type" plume). The most significant aspects of this phenomenon were that the plumes became very thin, under essentially no vertical diffusion, and could be found at large distances from their sources after one-night's travel (Brown et al., 1972). It was also realised that the observed plume behaviour reflected the properties of the atmospheric layers in which it became embedded.

These observations became more and more frequent in the early 1970s with the tracking of plumes from tall stacks. Measurement campaigns documented their travel distances to hundreds of km from the source (Millán and Chung, 1977; Millán, 1978; Carras and Williams, 1981). They also documented that stratified plumes could form and/or persist during the day, whenever conditions were right (Uthe and Wilson, 1979; Portelli *et al.*, 1982, Hoff and Gallant, 1985; Millán, 1987).

At about the same time, other projects documented the formation of extensive layers of ozone aloft (i.e. O₃ reservoir layers), at the regional scale in the US (Vaughan *at al.*, 1982) and at the urban scale in Europe (Varey *et al.*, 1988). In these cases convective venting of the boundary layer during the day formed the layers that became part of the "residual" boundary layer during the night. In fact, some of the early efforts to model regional air pollution transport in Europe were forced to become Eulerian and to include a residual (nocturnal) transport layer aloft to account for the observed SO₂ concentrations (van Egmond and Kesseboom, 1983 a; b).

Hot spots in the earth climate system

In recent years, different research projects around the world have demonstrated that the pollutant "exchange rate" between different regions and under different meteorological (and climatic) conditions is driven by interactions and forcings between different meteorological scales (Figure 1). Thus, for a believable evaluation of the impacts of anthropogenic emissions from urban to global scales, we need to implement within numerical models these spatial and temporal interactions together with the feedbacks among climate, regional air quality and transport (at local, regional and global scales).

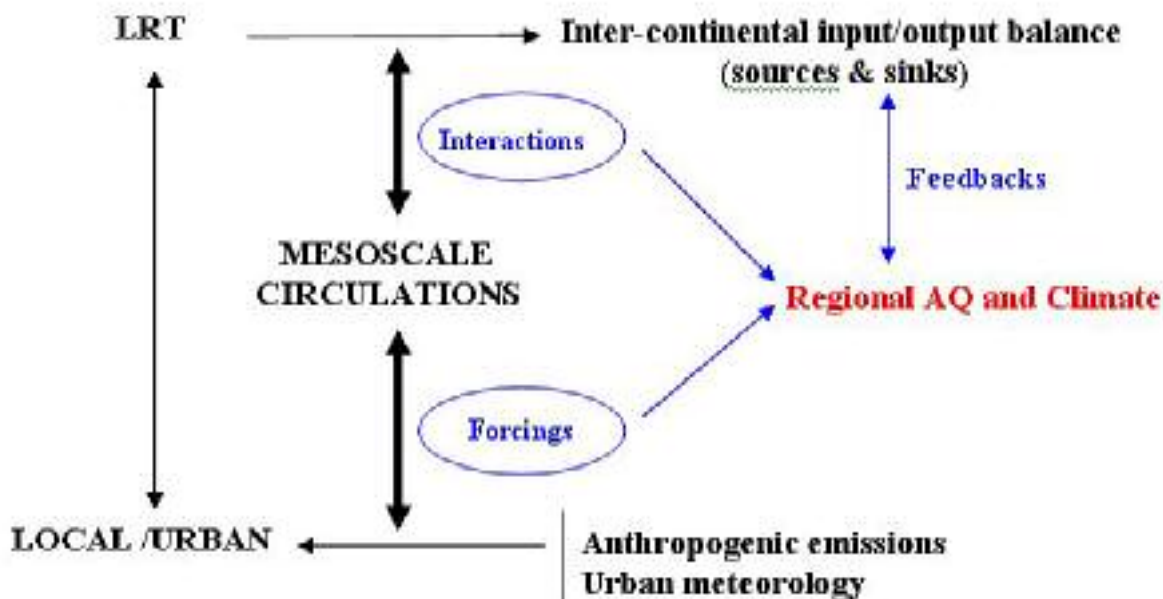


Figure 1. Feedbacks and interactions/forcings governing the real Long-range Transport of anthropogenic pollutants emitted at urban/local scales.

On the one hand, it is probable that the long-range transport (LRT) of aged air masses (on a global scale) has a significant impact on both regional quality (as satellite images show: Fishman *et al.*, 1990) as well as climate; on the other hand, deep convection in some regions (*e.g.* Spanish and Turkish central plateaus), or strong up-slope winds in others (*e.g.* Alps and Atlas mountains), can inject pollutants directly into the mid-troposphere (3 to 6 km) and even the upper troposphere (more than 10 km), participating in long-range transport processes (at regional, continental and global scales; Millán *et al.*, 1997).

Different scenarios have been identified for the transport of photo-oxidants and other pollutants within and outside of Europe (Millán *et al.*, 1997 ; Lelieveld *et al.*, 2000). One of the most significant experimental evidences is the tropospheric ozone anomaly detected systematically by satellite over the Mediterranean basin (Fishman *et al.*, 1990). This anomaly is the result of the interaction of different meteorological scales within this basin and is mainly attributed to the fact that the Mediterranean is a closed area surrounded by several high peninsulas and mountain barriers, and with a high increase of anthropogenic emissions in the area during the last years. The most significant features of the transport and transformation of pollutants (T&TP) in this area (in agreement with the aforementioned tropospheric ozone anomaly) are:

- (a) that the transport takes place at different heights and in almost opposite directions (Millán *et al.*, 1997),
- (b) that the atmospheric dispersion in the troposphere is driven by secondary circulations and compensatory mechanisms (Millán *et al.*, 1992; 2002; Salvador *et al.*, 1997),
- (c) that deep orographic venting and strong convective injections are key mechanisms governing pollutant exchange between the lower and middle-to-upper troposphere (up to 6-10 km) (Millán *et al.*, 1997; 2002),
- (d) that the regionally-linked vertical recirculation system produces a strongly layered structure over the sea and on coastal sites of the Western Mediterranean (Millán *et al.*, 1992 ; RECAP-final report, 2003), and
- (e) that, contrary to areas dominated by advection, modelling results have shown that the time period for renovating 80% of the air-mass below approximately 3500m in the Western Mediterranean Basin is of the order of 7 to 10 days (Gangoiti *et al.*, 2001),

although temporal scales for LRT are smaller than the residence time of primary air pollutants (or their secondary products) within the whole Mediterranean basin (Kallos *et al.*, 1998).

Thus, to address questions such as what is the budget at various scales of atmospheric pollutants and the LRT of regional air pollution, it is necessary to elucidate some scientific questions related to the aforementioned meteorological interactions. There are indeed indications that the formation and distribution of photo-oxidants in urban plumes, at regional or continental scale, in the boundary layer and in the free troposphere, are all linked together. Although the strength of these links is not yet known, experimental data and complementary modelling results from EC research projects (*e.g.* MECAPIP, RECAPMA and SECAP) established the links between atmospheric circulations from the local, through the regional, to the sub-continental scales, particularly in summer and in the central and western Mediterranean basins.

- To start, it is crucial to assess the contribution of deep orographic venting along the main mountain barriers to the import/export balances in Europe. Some of these mechanisms of pollutant injection to the mid-high troposphere have already been documented and some are postulated (Millán *et al.*, 1997 ; Kallos *et al.*, 1998). These mechanisms have special relevance not only for assessing air pollution balances but also for the chemistry to be used in the models (*e.g.* dry or/and wet phase). As published previously, in complex terrain it is necessary to use spatial resolutions of the order of 2 km to account for 95% of the terrain influence on atmospheric flows (Salvador *et al.*, 1999).
- The second important issue is the assessment of the compensatory mechanisms and secondary circulations which perturb the synoptic atmospheric flows. It is relevant to note that modelling the deep vertical exchanges requires carefully selected computational grids and that despite using the finest vertical resolution at the limit of numerical instability, it is still not possible to simulate the amount of compensatory subsidence (Millán *et al.*, 2002) or most of the fine layered structure observed experimentally. In relation to this second issue, current experimental and modelling evidences for the Mediterranean basin (Millán *et al.*, 2002) indicate the importance of the following aspects of compensatory mechanisms and secondary circulations: (a) their role in the aging of pollutants in the mid and lower troposphere, (b) their interaction with the general circulation (studying the mechanisms and strengths involved), (c) the daily evolution of the main input/output pathways, (d) the thin reservoir layers formation as a consequence of the compensatory subsidences, and (e) the entrainment mechanisms from the upper troposphere-lower stratosphere to the mid and lower troposphere.
- The third important question regarding the contribution of regional pollution to LRT is the characteristic residence-recirculatory times in the Mediterranean basin. Current modelling evidence for the Mediterranean basin (Gangoiti *et al.*, 2001) indicates that nesting of the near coastal recirculations within the regional scale results in longer recirculatory times (at least, 4.5 day return times).

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Ozone Production in Polluted Air Masses undergoing Long-range Transport

A contribution to ACCENT T&TP: Long-range Transport

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Measurements of nitrogen oxide (NO) and other trace gases over the N. Atlantic have been used to show that throughout much of the lower and mid-troposphere (LT and MT) during summer net photochemical loss of ozone (O_3) is occurring (Reeves *et al.*, 2002) (Figure 1).

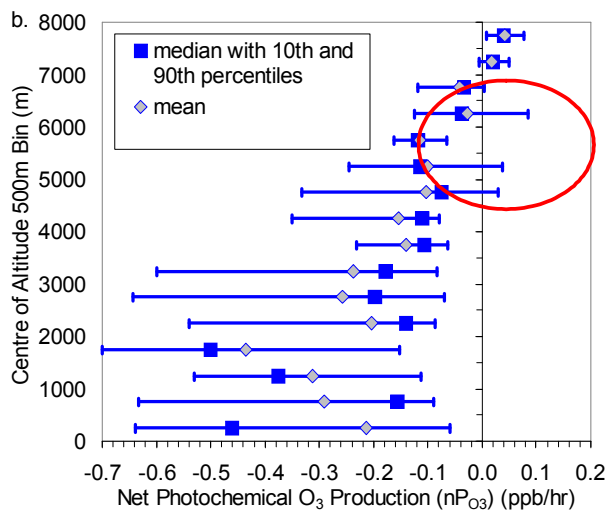


Figure 1.

Above about 7 km the NO concentrations began to slightly exceed the NO compensation point (i.e. NO concentration at which net photochemical production of O_3 is zero). This was partly because of an increase of NO concentrations with altitude, but also a decrease with altitude of the compensation point. This trend in compensation point is largely because of the decrease in water vapour leading to less photochemical loss of O_3 . Data collected over several seasons also shows a tendency for the NO compensation point to be higher in summer, when water vapour concentrations are higher. The vertical profile in NO is partly because of a shift in the NO/ NO_2 (nitrogen dioxide) ratio in favour of NO, due to increasing photolysis of NO_2 and with lower temperatures a decrease in the rate coefficient for the reaction of NO with O_3 to form NO_2 . Thus there is a tendency for O_3 transported in the upper troposphere (UT) to be photochemically maintained, whilst in the LT and MT it is likely to be destroyed. However, there are also several examples of polluted air masses, with elevated concentrations of NO, in the MT in which net photochemical production of O_3 was occurring (Circled in Figure 1, and illustrated in Figure 2).

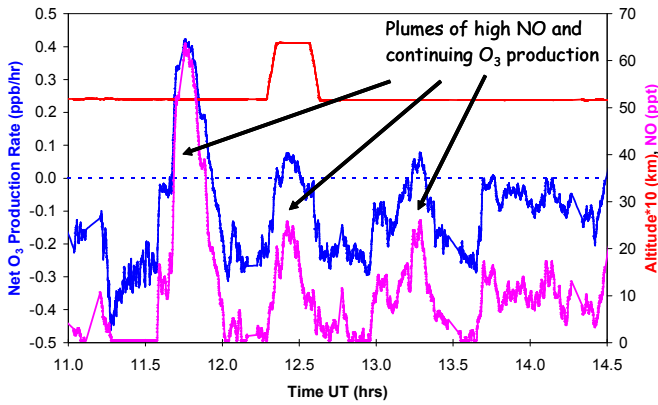


Figure 2.

It is still not known where much of the O₃ in the troposphere is formed. Is it formed in the polluted boundary layer and then transported into the free troposphere (FT) or is it produced *in-situ*? Comparing data collected over the mid-Atlantic with that over central Europe clearly illustrates that the photochemically production rates are far greater in the continental boundary layer (Figure 3).

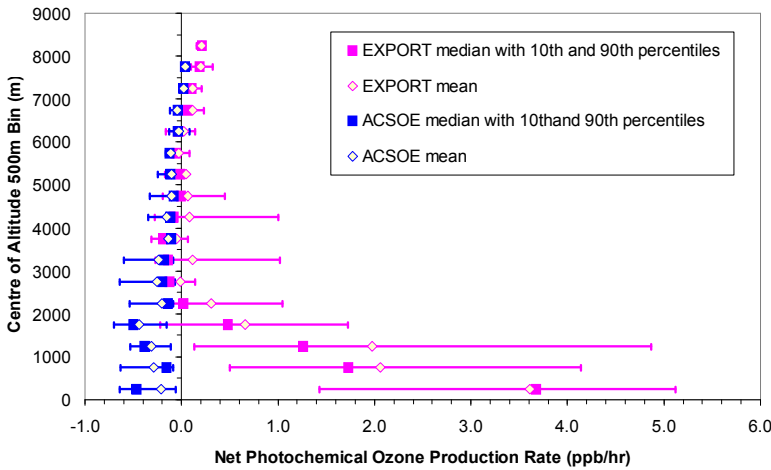


Figure 3.

How much of the O₃ that is produced there is transported to the FT before being deposited to the surface is not clear. Again there are examples of net photochemical production of O₃ occurring in MT. These are associated with a frontal system and pollutants being rapidly uplifted by convection embedded in a warm conveyor belt (Purvis *et al*, 2003). Also the tendency for net-photochemical production is again observed in the UT.

Recently data was collected over the North Atlantic as part of the ITOP project (Intercontinental Transport of Ozone and Precursors) in air masses polluted by forest fires in Alaska and Canada. In these plumes carbon monoxide (CO) concentrations were enhanced substantially (up to 500 ppb) (Figure 4).

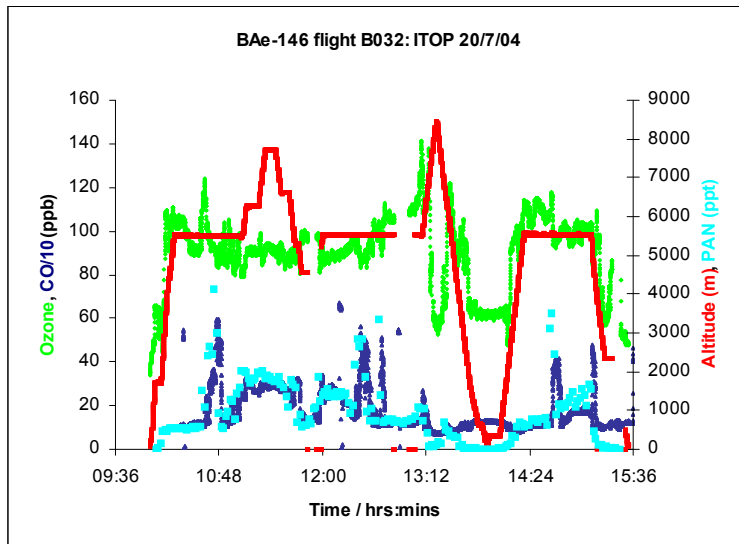


Figure 4.

Peroxyacetyl nitrate (PAN) concentrations were also elevated and for the most part were correlated to CO. However, O₃ were only slightly enhanced. The chemistry of this long range transported pollution plumes requires further examination.

Co-workers

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Transport of atmospheric trace substances investigated with the FLEXPART and FLEXTRA models

A contribution to ACCENT T&TP; Long-range Transport

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In the following, a short overview is presented of ongoing activities and plans at BOKU-Met which are related to the agenda of the ACCENT topic of transport and transformation. All of this work is at least partly based on FLEXPART and FLEXTRA models (more about these models see below). Not included in this list is work related to work with chemistry-transport models. BOKU-Met is also active in urban- and regional-scale modelling with the MM5-CAMx modelling chain (this work was presented in the ACCENT workshop at Paris, June 2004).

Evaluation of transboundary nuclear risks

The most recent activity is a mapping of the risk to Austria from a potential nuclear accident at any location in Europe. It uses a combination of FLEXPART LPDM (detailed forward calculation for all the nuclear power plant sites in Europe and 88 dates had been made in a previous project) and FLEXTRA trajectory output (using Europe-wide gridded residence times produced from backward simulations with trajectories starting every 6 hours). The trajectory data are used to spatially interpolate the LPDM data based on the flow climatology.

Source-receptor matrix calculations for the monitoring of the Comprehensive Nuclear-Test-Ban Treaty CTBT (global scale). This is an ongoing activity in cooperation with the CTBTO International Data Centre and the Austrian Meteorological Service, as National Data Centre for the CTBT.

Source-receptor relationship calculations for air pollution and GHG monitoring. Small projects have been carried out / have been submitted for funding to investigate source regions for aerosol in Austria. A cooperation with Hungary concerning the GHG measurements at the Hegyhatsel high tower will commence soon in the framework of our Marie Curie Training Site with a fellow from Budapest.

Inverse modelling for CTBT, air pollution, GHG

Volcanic ash simulation and data assimilation for VAAC purposes (idea and first tests)

Synoptic classification based on back trajectories for climate-change related activities. Clustering of back trajectories from Austria has been used to identify synoptic situations producing heavy precipitation in different regions of Austria. Application to GCM data is still pending.

Quantification of uncertainties in transport modelling. This is a major project, the proposal is still under review. We consider this topic to be of major importance in the future of long-range ATM. See contribution at the June 2004 Paris workshop for more details.

Improved, structure-conserving temporal interpolation algorithm for use in off-line atmospheric transport modelling. A proposal for this project is to be submitted soon in cooperation with the Faculty of Mathematics at the University of Vienna.

More information on ongoing work including publications can be found on our web pages <http://www.wau.boku.ac.at/met.html>

Suggestion: FLEXTRA and FLEXPART as (ACCENT) community models

We are making a suggestion to promote the FLEXTRA trajectory model and the FLEXPART regional-scale Lagrangian particle dispersion model as community models for ACCENT or the European scientific community in general.

Background

One of the basic ideas for the FP6 Network of Excellences is to share facilities, tools, data, *etc.*, so that each group can concentrate on their own main strengths and make use of other groups capabilities as support.

There is an obvious need for atmospheric transport modelling and related data evaluation by many measurement-oriented groups. This can be recognised for example through the fact that NOAA ARL's web-based on-line ATM tool with HYSPLIT (<http://www.arl.noaa.gov/ready.html>, principal scientist: Roland Draxler) is used also by European research groups. The success of READY is a clear demonstration of need for such a tool. One may ask, why create another tool if this one already exists? Answers include that for Europe, other meteorological input data (ECMWF, limited-area models) may provide better accuracy, that each of the models has specific features and that it will be good if there is an alternative. Another point is that I think an offer of personal support (conditions of which have to be developed) is quite an important matter, because not everybody has the scientific background to make the optimum use of the possibilities. We have here at BOKU a good deal of experience with helping colleagues from other disciplines to obtain and work with meteorological data. This kind of cooperation would also be very much in line with the basic idea of Accent as a Network of Excellence.

The FLEXTRA trajectory model and the FLEXPART Lagrangian particle model (which has a receptor-oriented mode, a necessity for application in combination with chemical monitoring data) was originally developed in our group (Andreas Stohl, Gerhard Wotawa *et al.*). The models are already freely available on the web and used by many groups worldwide. ACCENT could be a platform to further promote these models especially in the European research community, to facilitate access to them, and to further improve them. Since Andreas Stohl has left our institute, the further development has been carried out in a cooperation between us. After spending several years in Munich, Andreas Stohl is presently at NOAA AL in Boulder and will soon join NILU in Oslo, so that there is a good chance to continue this cooperation also within ACCENT. If this suggestion is positively received by the ACCENT community, all involved and interested parties should set up a detailed plan. The following section gives some first, personal ideas of what should be done.

Possible building blocks and activities

- Create web-interface for self-service trajectory and LPDM s-r calculations similar to NOAA-ARL tools: needs a server platform, some programming, and data base of gridded meteorological analyses (ECMWF? legal issues? European alternatives? LAMs?)

- Offer personal support (This seems to be important as often, measurement-oriented people use only sub-optimal transport calculations, or have only limited experience with evaluation modelling data in combination with chemical monitoring data.)
- Continue to improve these tools, especially FLEXPART. Some ideas:
 - parallel version (possible cooperation with Univ. of Salzburg, Dept. of Scientific Computing)
 - better multi-scale capabilities through nested and adaptive output grids
 - improved numerical algorithms (see our interpolation project)
 - improved physical parameterisations (convection, ongoing work will be continued by C. Forster; usage of modelled TKE; ABL venting; better wet scavenging

Many more possibilities exist which we can explore.

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Atmospheric Long-range Transport and its Impact on the Trace-gas distribution in the Free Troposphere over Central Europe (ATMOFAST)

A contribution to ACCENT T&TP; Long-range Transport

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Within the German ATMOFAST project (emerged from the European projects VOTALP and STACCATO) lidar sounding of O₃, aerosol and, starting in 2004, water vapour, as well as measurements of O₃, ⁷Be, humidity and CO at the Zugspitze summit (2962 m a.s.l.) are combined with numerical simulations with the FLEXTRA, FLEXPART and EURAD models to evaluate the major transport pathways, the principal source regions and the chemical transformation of the air masses imported from outside Europe. In the focus of the activities are stratospheric air intrusions, intercontinental transport from North America and eastern Asia, Saharan dust, fire plumes and advection of low-O₃ air from the remote Atlantic.

Stratospheric air intrusions have been characterized with the lidar measurements and model calculation in some detail. So far, vertical sounding has been performed during more than 60 intrusion periods. In particular, during the period between February and August 2001 each of the 17 forecasted intrusions were captured with the lidar. A particularly complex case (June 20-21, 2001) was used for model validation (Zanis *et al.*, 2003; Roelofs *et al.*, 2003). It was shown by FLEXPART modelling that the ECMWF data allow the observed structures to be reproduced in great detail. The discrepancies seen for quite a few other model simulations must, therefore, be ascribed to the limited spatial resolution chosen and specific problems of the individual models.

Filtering the Zugspitze data back to 1990 has yielded the strongest positive ozone trend at 3000 m for air masses descending from the upper troposphere and lower stratosphere (Scheel, 2002). This positive trend, which goes in line with the increase of the ⁷Be values since the mid-seventies, seems to mask a downward trend in lower-tropospheric ozone expected due to the reduction in European precursor emissions since 1990, perhaps together with a growing background of East Asian origin. In fact, the overall ozone trend at the Zugspitze summit between 1990 and 2002 is even slightly positive, whereas that for the nearby Wank station (1780 m a.s.l.) is approximately constant. This is in some agreement with the observation that more than twice as many stratospheric intrusions reach 3000 m than 1800 m. The only sign of the shrinking European emissions is a decreasing amplitude of the seasonal cycle in the Wank ozone data.

Anthropogenic ozone from North America influences the central European boundary layer only in rare cases. These contributions (80-110 ppb) pass over our area typically between 4 and 11 km a.s.l. (*e.g.* Trickl *et al.*, 2003). This is ascribed to upward transport of the polluted air masses in the warm conveyor belt of frontal systems both over the United States and/or the Atlantic Ocean, followed by rapid transport in the jet stream. The EURAD simulations have shown some of the details of the chemical transformation of the polluted air masses. As expected, most changes in air composition take place during the export from the North American boundary layer.

Some puzzling very dry layers with up to 150 ppb of ozone, in part as thick as 6 km, were recently attributed to mixed input from East Asia, the U.S. and most likely the stratosphere over the Pacific Ocean in a rapid air stream (James *et al.*, 2004). The details of the mixing of the different contributions are not yet fully analysed.

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Influence of Long-range Transport and Local Sources on Aerosol Formation and Growth in the Boundary Layer

A contribution to ACCENT-T&TP: Long-range Transport

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Long-term measurements have shown that the appearance of ultrafine particles detected at few nanometers and their subsequent growth to about 100 nm are frequent process under continental and marine conditions as well as in the free troposphere. The observations done at different European locations have included a remote boreal forest (1); Helsinki suburban area (2); an industrialized agricultural area in Finland (3); and a mountain site in Germany (4); Iso coastal environment, *etc.* Due to its location, our Environmental Research Station in Preila (located on the Curonian Spit, which separates the Curonian Lagoon and the Baltic Sea) provides an ideal natural 'laboratory' to study new particle formation and growth processes.

Our experimental results showed that aerosol nucleation appeared on the same days over large areas (some hundred kilometers distance) suggesting that the process can extend from microphysical to synoptic scale. It has been found that nucleation events are related with high values of solar radiation and low concentration of pre-existing particles. Also, the nucleation events were associated with air masses coming from N-W and N-E directions. Experimental results revealed that some nucleation events are related with air mass transport from North Sea (long-term events). Short-term events occurred when backward air mass trajectory analysis showed that they came from central and western Europe. Also, some clear nucleation events were observed during days when mean daily concentration of SO₂ or NO₂ was two or even three times higher than mean month concentration. It has been found that local meteorological conditions can influence particle formation. During the one of group events of increasing number concentration of nucleation mode particles caused increase in particle growth rate. Possibly the oxidation of DMS occurred mostly via abstraction way and predominantly H₂SO₄ particles were generated. While during the other group of events, growth rate of accumulation mode particles decreased with increasing nucleation mode particle number concentration. This result supports the hypothesis that observed difference in the particle diameter growth rates can be explained by the differences in the particle surface chemical composition. As the organic chemistry obviously was involved in the formation of the nucleation mode particles, these particles attached on the surface of larger particles and formed organic film, which limited water vapour condensation during the another group of events.

The objectives of this project is to set up continuous aerosol size distribution measurements together with measurements of basic meteorological parameters and certain gas components to the Lithuanian Environmental research station in Preila. It will be determined the source strength of new particle formation and growth in Lithuanian coastal environment. Influence of long-range transport, local sources including biogenic emission will be investigated. The specific objectives are: 1) to understand chemical and physical pathways leading to homogeneous nucleation of new particles; and 2) to understand the meteorological conditions required for the nucleation events and growth.

The size distribution will be measured using continuous aerosol size distribution measurements together with measurements of basic meteorological parameters and certain gas and aerosol components. The size distribution measurements include Differential Mobility Aerosol Spectrometer ELAS-5Mc (Institute of Physics) and Optical Aerosol Spectrometer (Institute of Physics) covering the size range of 10-300 nm and 0.3–10.0 μm , respectively. Spectrometers enable to record of aerosol size spectra in 15 minute intervals. The meteorological parameters temperature, relative humidity, wind speed and direction and solar radiation will be measured. Also, the gas components include NO_2 , SO_2 , NH_3 , O_3 will be determined. The measurements will be set from December 1, 2004 in Preila. Also, the software tool PloTra for air mass trajectory data visualisation and analysis will be used, the pollutants (SO_2 , NO_2 , O_3 and other) database from the station Preila will be examined.

The results obtained from the long term measurements will be used for parametrization of nucleation and growth events for long-range transport models.

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9.3 Chemical Weather

THOR – an Integrated Air Pollution Forecasting and Scenario Management System

A contribution to ACCENT-T&TP: Chemical Weather

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The comprehensive and unique model system THOR, developed at NERI, includes several meteorological and air pollution models capable of operating for different applications and at different scales. The system is capable of accurate and high resolution three-days forecasting of weather and air pollution from regional scale over urban background scale and down to individual street canyons in cities – on both sides of the streets. The coupling of models over different scales makes it possible to account for contributions from local, near-local as well as remote emission sources in order to describe the air quality at a specific location - *e.g.* in a street canyon or in a park. The system can be used in connection with, for example, urban and rural monitoring programs. Furthermore, the system can be used to forecast air pollution from accidental releases such as from power plants, industrial sites and natural or human made fires.

The THOR system can be applied for forecasting, nowcasting, retrospective analysis and air pollution assessments and management. The system can furthermore be used for information and warning of the public in cases of high air pollution levels and for policy management (*e.g.* by emission reduction or traffic scenarios) of many different chemical compounds. The system can be applied operationally for any location all over the world. The system consists of several different air pollution models – all developed at NERI during the last decades. A schematic diagram of the different modules and the data flow chart of the THOR system is shown in Figure 1.

Applications of the THOR system

Present capabilities of the THOR system include all aspects within forecasting, nowcasting, supplement to monitoring programs, scenarios, retrospective analysis, assessment and management of air pollution.

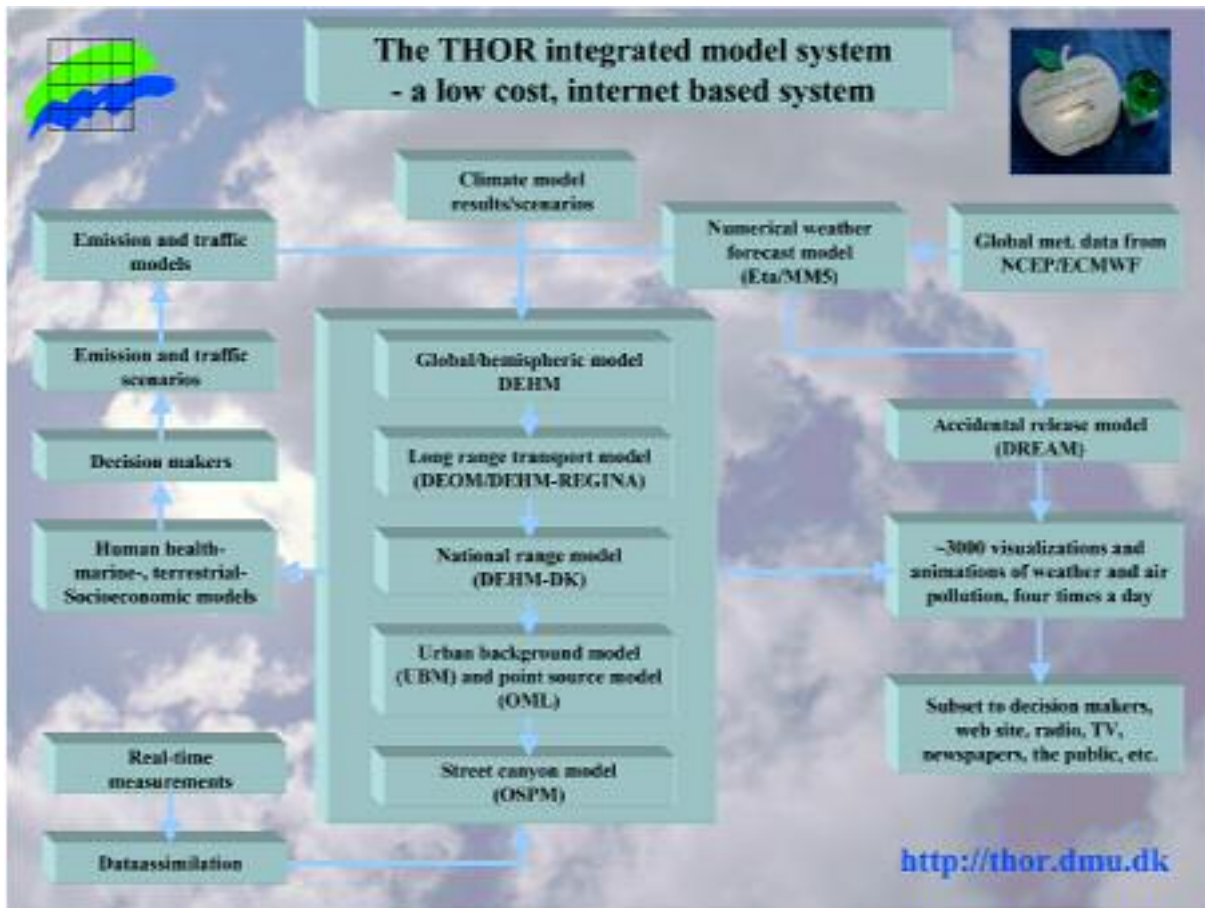


Figure 1.

Some examples are:

Three-day high-resolution regional weather forecasts.

Three-day regional air pollution forecasts of 61 chemical compounds, e.g. nitrogen-oxides, ozone, volatile organic compounds, sulfur and sulfate, ammonia and ammonium, nitrate, particles, *etc.*

Three-day urban background air quality forecasts in specifically identified cities for example, nitrogen-oxides, ozone, benzene, carbon monoxide and particles.

Three-day urban air quality forecasts at street level – at both sides of the streets for the same chemical compounds as in the urban background.

Three-day forecasts of accidental releases into the atmosphere from *e.g.* nuclear power plants, fires, chemical industries, *etc.*

Long term runs over several decades for assessment and scenarios.

Coupled to socio-economic models, marine models, models for human exposure and climate models.

Emission and traffic reduction scenarios for air pollution management and decision making.

Multiple-point and area source dispersion modelling, for determining the effects on air quality caused by proposed new emission sources (*e.g.* new power plants, chemical industries, commercial activities).

Automated production of data, visualizations (maps and time series), information and warnings.

Data, forecasts and warnings are disseminated to the authorities and decision-makers.

Data can be disseminated to the public via the Internet or other media.

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Data Assimilation for Chemical Weather Forecasting

A contribution to ACCENT-T&TP: Chemical Weather

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The data assimilation group of the Rhenish Institute for Environmental Research (RIU) at the University of Cologne focus on the optimal exploitation of observations by combination with other information sources like chemistry transport models and climatological information. The objective is to infer a chemical state analysis, specifically a chemical weather state, as precise as possible. While this is a practical basis for integrating chemistry transport models a better way, producing more reliable forecasts based on more reliable initial values, chemical state analyses of the atmosphere are of interest of its own right and helpful in many way: To name but a few items, budget assessments with hardly observable tracer fluxes, and exposure time estimates will be more reliable, while scientific field campaigns can be complemented with an additional wealth of external data, in combination with chemistry transport models. The underlying model system used at the RIU group is the EUROpean Air pollution Dispersion model EURAD.

The general methodology rests on advanced data assimilation algorithms, most prominently the four-dimensional variational technique (4-D var). With this method it is possible to ingest direct and remote sensing observations, scattered in space and time, into a model based data assimilation system. Most prominently, recently available tropospheric satellite data can be assimilated, even when only given in terms of tropospheric columns, as in the case of NO₂. The research focus for chemical weather forecasting is placed on multi-scale forecasts, starting with a European scale grid mostly 54 km horizontal resolution, down to a third or fourth generation nested grid, with 2 km resolution.

Initial values are not necessarily the least known parameter. Rather, the emission rates are also considered as insufficiently known, while, at the same time, exerting a strong influence on the chemical evolution. Consequently, the flexibility of the variational approach is and will further be used for emission rate related inversions.

The EUAD data assimilation system will be used to support measurement campaigns, focussed both on surface level and aircraft campaigns. A suite of presently ongoing studies include the following objectives: boundary layer ozone formation (postprocessing BERLIOZ), updrafted pollutants in cyclonic warm conveyor belts (CONTRACE), upper tropospheric chemistry (SPURT), and others. In nearly all cases, the use and benefits of satellite retrievals will be assessed, namely NO₂ tropospheric columns and NNORSY neural network based ozone profiles.

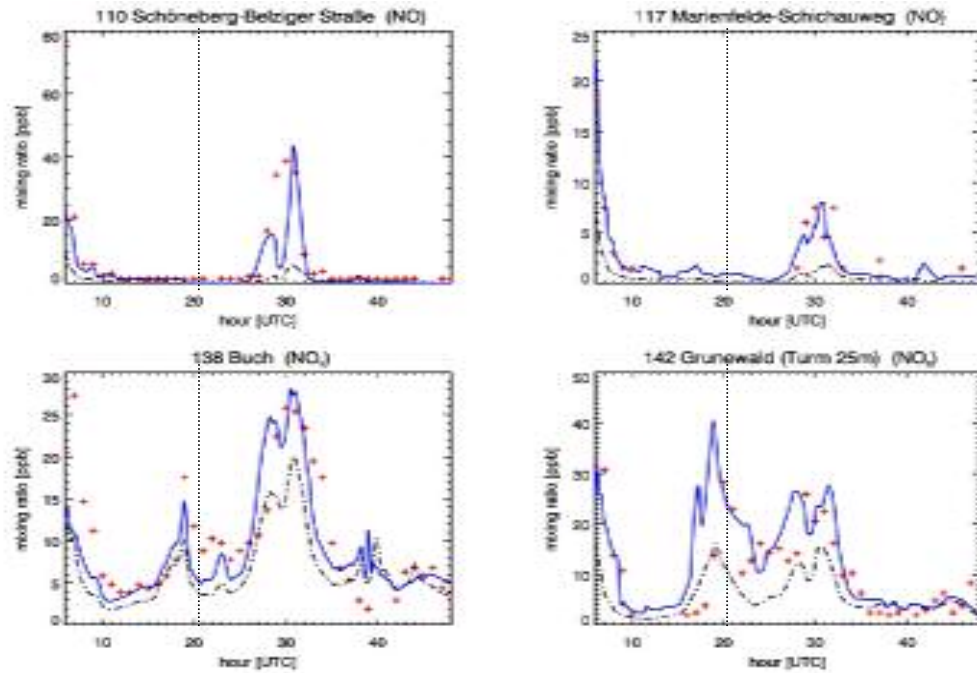


Figure 1. Comparison of CTM prediction skill for urban NO (top row: Berlin stations) and NO₂ (bottom row, Berlin outskirts station) forecasts during the BERLIOZ campaign 1998. Shown forecasts without (dash-dotted black line) and with (blue line) 4-D-var assimilation with emission inversion. Only observations (red crosses) from 6:00 to 20:00 UTC are assimilated (left of dotted vertical line), observations from 20:00 UTC, July 20th to

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Stratospheric Ozone Forecasts, Satellite Observations of the Tropospheric Composition and GMES

A contribution to ACCENT T&TP: Chemical Weather

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In this contribution I discuss several aspects relevant to chemical weather, based on activities in the "atmospheric composition" section of the KNMI.

Stratospheric ozone and UV forecasts

Ozone data assimilation has received increasing attention over the past years. This development is related to vertical extensions of numerical weather prediction (NWP) models, including the full stratosphere. Several major NWP centres, like the European Centre for Medium Range Weather Forecast (ECMWF) and National Centres for Environmental Prediction (NCEP), have started programs for the assimilation of satellite ozone data, and stratospheric chemistry-transport models have been very successful. In particular assimilation-based reanalysis runs that include ozone as prognostic variable are very valuable for atmospheric chemistry research, protocol monitoring and NWP itself. Studies show that NWP systems are well able to describe synoptic-scale features and short term variability. Forecasts of ozone anomalies are meaningful up to 7 days in advance. This is of importance for an accurate description of UV radiation levels and chemistry in the troposphere, and for surface UV predictions (*e.g.* clear-sky or UV index). For instance the large UV values resulting from oscillations of the ozone hole in October and November can be well predicted. Several satellite data sets are available in past, present and future to guarantee accurate reanalyses, analyses and forecasts of stratospheric ozone.

Satellite observations of the troposphere

Several limb and occultation satellite sensors (*e.g.* the UARS mission) have provided detailed information on the stratospheric composition and chemistry responsible for ozone depletion. For the troposphere and for chemical weather applications the amount of observations is much more limited. MOPITT on EOS-TERRA is providing CO observation in the lower free troposphere and initially had a profiling capability as well. Several satellite instruments are used to derive optical properties of aerosols in the lower troposphere. The UV-Vis nadir viewing spectrometers GOME on ERS-2, SCIAMACHY on ENVISAT and OMI on EOS-AURA have capabilities to provide tropospheric ozone, NO₂, SO₂, CH₂O and aerosols, key compound in tropospheric chemistry. SCIAMACHY in addition measures CO and methane, and greenhouse gases.

Especially the NO₂ data sets are of considerable importance, given that the formation of ozone in the troposphere is often NO_x limited. Due to the short residence time of NO_x in the atmosphere the observed high tropospheric column values occur close to major NO_x sources. Issues related to the use of these measurements for chemical weather applications are:

- Quantitative tropospheric retrievals are needed. The retrieval of the tropospheric column is very sensitive to accurate knowledge of the cloud cover, high-quality surface albedo maps, knowledge of the NO₂ profile shape in the troposphere and

accurate estimates of the stratospheric background including synoptic-scale variability.

- High resolution measurements with a high repetition rate are important. GOME has a footprint of 320×40 and global coverage in three days, and is able to resolve regional-scale variability. For SCIAMACHY this is 60×30 km and global coverage in 6 days. SCIAMACHY is able to resolve the contribution of major cities. However, due to the 6-days and because NO_x can not be retrieved below clouds, new information is available roughly once per month. OMI will improve on both GOME and SCIAMACHY with small pixels, 24×15 , and a global coverage each day (more than one measurement/day over Europe). OMI was launched July 2004, and the first results are expected soon. A near-real time delivery of OMI NO_2 is foreseen.
- For data assimilation purposes the retrieval product should contain realistic error estimates and averaging kernel (sensitivity profile) information. The latter will remove the a-priori dependence of the retrieval during the assimilation and for comparisons with models.
- Advanced data assimilation schemes are needed, e.g. 4D-Var or Kalman filter. These approaches are able to transfer the information of the concentrations of short-lived NO_x to e.g. improved emission estimates.

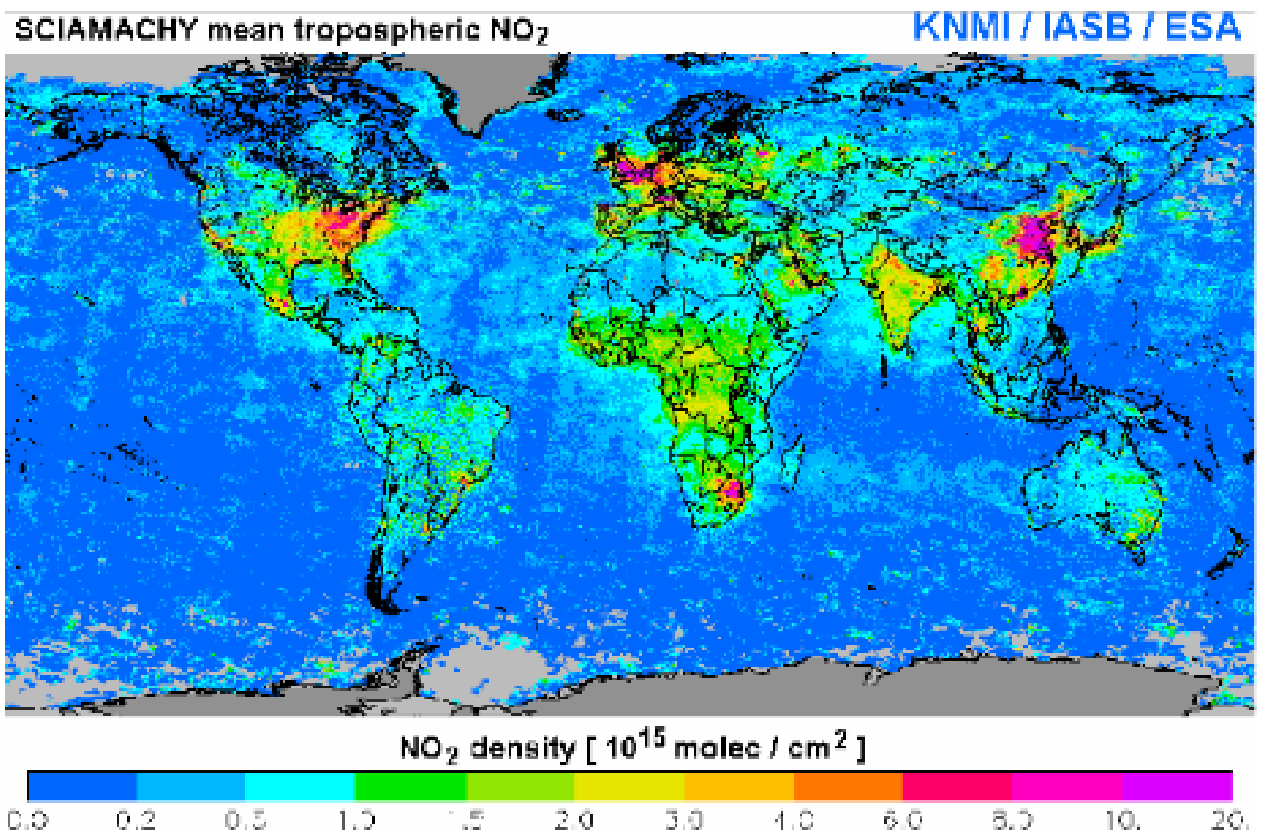


Figure 1. Global yearly mean tropospheric NO_2 columns for 2003, measured with SCIAMACHY. Retrievals performed by BIRA/IASB and KNMI (data available on <http://www.temis.nl/>)

GMES and chemical weather

Two new projects in the Global Monitoring of Environment and Security (GMES) are of direct relevance to the development of chemical weather capabilities and interface to users and the public. These are GEMS and PROMOTE. Many of the regional and global scale European models are involved in these projects, and European activities related to chemical weather and the interaction with users will be coordinated through these projects.

GEMS is a European Union Integrated project which is currently under negotiation. The project is coordinated by ECMWF. The aims of GEMS are:

- To set up an operational capability for global-scale high resolution analyses and forecast of the atmospheric composition, including reactive gases, aerosols, greenhouse gases.
- To provide re-analyses and analyses based on (all available) satellite, ground-based and airborne observations
- To provide boundary conditions for regional/urban scale air-quality modelling and forecast systems

The GEMS system is projected to become operational in 2008. The IGACO system, as sketched in the IGACO report, has many aspects in common with GEMS and GEMS is envisaged to provide an important contribution to it.

PROMOTE (PROtocol MOniToring for the GMES Service Element) is the atmospheric sub-project of the ESA GMES Service Element, co-ordinated by the KNMI. Its mission statement is: "To deliver the Atmosphere GMES Service Element: To construct and deliver a sustainable and reliable operational service to support informed decisions on the atmospheric policy issues of stratospheric ozone depletion, surface UV exposure, air quality and climate change." PROMOTE proposes and implements GMES services relevant to the ozone layer, UV-exposure on the ground, air pollution and climate change. These services are directed at the needs for information on environment and climate by public authorities and governmental agencies. Some services are directed at the general public, while interest from Industry has been found in the energy and health sector.

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Application of Functions influencing Air Pollution Problems

A contribution to ACCENT T&TP: Chemical Weather

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The functions of influence are solutions of an equation adjoint to the pollution transport one. They depend on the meteorological conditions, on the domain, which pollution has to be estimated, and on the choice of the air pollution characteristic (for example time/space averaged concentration in the chosen sub-region and in particular different countries; wet and dry depositions in the chosen sub-region; pollution fluxes through the side boundaries of the chosen sub-region and in particular through the different countries borders; any kind of loads on soils or vegetation; etc.) but not on the air pollution sources. Thus if the functions of influence are known for a chosen domain and pollution characteristic, the pollution characteristic value can be easily obtained for arbitrary pollution sources. In particular the functions of influence can be applied for discrimination of the contribution of each of the pollution sources to the air pollution of the chosen region. An important application of the functions of influence is also for optimization of the location and working regime of existing or planned new sources and building up different emission reduction strategies.

The functions of influence can be perceived as Eulerian analog of the back-wind trajectories, so they produce a rather graphic and informative idea also of the integral meteorological conditions under which the studied pollution characteristic are formed. All these properties made them a popular and useful tool in the air pollution studies, especially when computer resources limitations have to be also considered.

The functions of influence had been originally defined for the case of linear chemistry as solutions of an equation conjugated to the pollution transport one. As the chemical models become more and more complex, the formulation of the problem of the functions of influence for the case of non-linear chemistry is important and indisputably necessary from practical point of view. Some speculations on possible approximations and approaches in this sense are suggested.

The presentation aims at giving a general idea of the functions of influence problem and its application to air pollution and environmental problems, including:

- a general formulation of the problem;
- a numerical treatment by using the splitting-up method;
- an application of the functions influencing pollution abatement strategies and model sensitivity studies;
- an application of the functions influencing data assimilation; and
- some examples from particular studies.

Research Interests Overview

A contribution to ACCENT T&TP: Chemical Weather

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The overall focus of my research is modelling of the chemical weather and its short- and long-term modifications. For the last four years I have been leading a government-sponsored junior research group, which has allowed me to develop a broad perspective and good working knowledge of a wide range of issues involved in chemical weather modelling, and an in-depth expertise in several of its sub-fields.

My current and planned future research involves three basic components of chemical weather modification modelling. These are outlined below, along with references to my past experience on these topics:

Basic model development

Transport routines, especially deep convection (Lawrence and Rasch, 2004; Salzmann *et al.*, 2004; Rasch and Lawrence, 1998; Jöckel *et al.*, 2002)

Chemical mechanisms (Lawrence *et al.*, 1999a; von Kuhlmann *et al.*, 2003a; Bonn *et al.*, 2004)

Precipitation scavenging and dry deposition (Lawrence and Crutzen, 1998; Crutzen and Lawrence, 2000; Lawrence *et al.*, 1999; von Kuhlmann *et al.*, 2003a; plus evaluations of the model hydrological cycle in Lang and Lawrence, 2004)

Emissions (adaptation and implementation of established databases in Lawrence *et al.*, 1999; von Kuhlmann *et al.*, 2003a,b)

Process studies

Effects of transport processes, especially deep convection and intercontinental transport (Lawrence *et al.*, 2003a,b; Lawrence *et al.*, 1999b)

Effects of continental anthropogenic emissions, especially related to Asian regions (Lawrence *et al.*, 2003a,b; Lal and Lawrence, 2001; Lelieveld *et al.*, 2001, 2002; Kunhikrishnan and Lawrence, 2004; Kunhikrishnan *et al.*, 2004a)

Effects of biomass burning emissions (Kunhikrishnan *et al.*, 2004b)

Effects of biogenic forest emissions (von Kuhlmann *et al.*, 2004; Bonn *et al.*, 2004) and oceanic emissions (Lawrence, 1993)

Emissions of nitrogen oxides from lightning and their effects (Lawrence *et al.*, 1995; Labrador *et al.*, 2004a,b)

Effects of emissions from ships (Lawrence and Crutzen, 1999; von Glasow *et al.*, 2003) and aircraft (long-term involvement in MOZAIC; Law *et al.*, 2000)

Chemical weather forecasting

Measurements campaign planning (Moore *et al.*, 1999; Lawrence, 2001; Lawrence *et al.*, 2003; my group was the first worldwide to produce global chemical weather forecasts of

O₃, CO, and other pollutants, tested during INDOEX in early 1999, with routine daily forecasts being operational since June 2001)

Long-term chemical climate forecasts and chemical weather change scenarios (ongoing work in my group, focusing particularly on changes related to Asian emissions, global megacity emissions, and on changes in the atmospheric reactive nitrogen cycle; also includes participation in the current round of IPCC scenario runs)

Agricultural planning and human health issues (practical applications of chemical weather forecasts for agriculture are still several years in the future; we have initiated a long-term collaboration with the Indian Department of Science and Technology to pursue this, with a guest from the Indian National Center for Medium Range Weather Forecasting joining our group again this past summer; we do not yet work on human health issues but it is likely to be an eventual area that we will get involved in with our forecasts, particularly in terms of the influence of long-range transport on regional pollution levels)

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Shipping as a source of NO_x at Weybourne

A contribution to ACCENT T&TP: Chemical Weather

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Several experiments have been carried out at the Weybourne Atmospheric Observatory to study regional photochemistry. These began in November 1993 and the latest one was held in May 2004. A consistent feature of all these experiments, which have become more comprehensive with regard to number of chemical species measured, is the large variation in NO_x in clean air sectors when the wind is coming in off the sea.

Clean air concentrations of many species including halocarbons and hydrocarbons at Weybourne are very similar to those experienced at Mace Head and other Northern Hemisphere background sites. The conclusion has been reached therefore that the large spikes in NO_x observed when the wind comes off the sea are produced by shipping.

NO_x records for Weybourne during the TIGER campaign in June 1995 and in the INSPECTRO campaign in September/October 2002 are shown along with wind direction for the former case. The largest excursions are observed when the wind is slightly north of east which would bring air from the main shipping lane down the North Sea to Weybourne (28 June 1995). The excursions range from about 2 ppbv to 15 ppbv and they result in an increase in background NO_x imported into the UK of the order of 1000 %. The consequences of this large source offshore must be substantial for background NO_x and hence ozone production along the east coast of the UK.

9.4 Chemistry Climate Interactions

Chemistry and Climate at the University of-Maryland

A contribution to ACCENT-T&TP: Chemistry Climate

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Contributions on transport and transformation of pollutants from the University of Maryland group involve recent findings on the N budget, the role of PBL dynamics and convection in smog and haze events, large scale dynamics, and uncertainty in emissions from biomass burning and from the developing world. These topics all contribute to the interaction of atmospheric chemistry and meteorology and to the link between local air pollution, intercontinental transport, and climate change.

Planetary Boundary Layer

Recent aircraft measurements during a multi-PBL day smog and haze event over the NE US indicated a clear role for two distinct reservoirs for air pollution. The PBL is characterized by high concentrations of primary pollutants such as CO and SO₂, modest levels of O₃, relatively low potential temperatures, and externally mixed aerosols. The lower free troposphere (LFT) is characterized by higher concentrations of O₃, larger, more internally mixed aerosols, greater potential temperatures, and greater intensity of UV radiation. Concentrations of pollution near the surface may well be controlled to a large extent by mixing between these two reservoirs. Pollutants in the LFT have a higher probability of long-range transport (Taubman *et al.*, JAS., 2004) including transport to Europe. Image Attached.

Results from the Blackout study (Marufu *et al.*, 2004) suggest the possibility of a larger role in smog chemistry for NO_x emitted by power plants, perhaps because these sources inject more into the LFT than do vehicles.

Convection

Evidence is increasing that mid-latitude convective clouds can inject water and pollutants into the lower stratosphere. This could perturb the photochemistry and radiative balance of this region of the atmosphere where greenhouse forcing is most effective (Poulida *et al.*, 1996; Fromm and Servranckx 2003; Hegglin *et al.*, 2004; Dessler 2004). This mechanism also transports pollution from N America to Europe.

Developing World Emissions

Estimates of emissions are generally uncertain, but particularly so for processes in the developing world. For example, bottom up estimates of emissions of black carbon (BC) from S Asia suggest less than 1.0 Tg/yr, while atmospheric observations downwind of India suggest 2-3 Tg/yr (Dickerson *et al.*, 2002; Guazzotti *et al.*, 2003; Habib *et al.*, 2004). Climate change models and chemical weather forecast models can not hope for reliability until these emissions are better understood. In international effort is required.

Biomass Burning

Observations made in the plume of the Quebec forest fires showed that the smoke has a profound impact on the radiative balance and can induce local heating sufficient to self stabilize and increase the range of influence. Smoke located above urban haze can generate particularly high levels of secondary pollutants. Aircraft, ground-based and satellite measurements of the radiative properties, however, disagreed as to the nature of the optical properties and radiative forcing (Taubman *et al.* 2004; Vant Hull *et al.*, *JGR.*, in press 2004).

Nitrogen Budgets

Recent investigations reveal that the Earth is likely to undergo profound increases in N deposition. Agricultural processes and animal feeding operations in particular are likely to contribute to these changes, with much of the growth coming from the developing world. These changes in the global N cycle may lead to climate and ecological problems such as increased PM loadings and reduced biodiversity (*e.g.*, NRC, 2002).

Motion of Jetstreams

Stratospheric ozone column contents as measured by satellite-borne TOMS instruments fall into coherent meteorological regimes, characterized by the position of the subtropical and polar jetstreams. The position of these jets appears to have moved poleward in the record of the measurements, 1979-present. This suggests a combined chemical and meteorological explanation for the observed reduction in stratospheric ozone between 25 and 60 degrees; the expansion of the tropical meteorological regime is consistent with observed tropospheric temperature changes (figures provided; Hudson *et al.*, 2003, Andrade, 2004).

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Development of Emission Strategies using an Advanced Aerosol Model

A contribution to ACCENT-T&TP: Chemistry Climate

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Particulate and gas-phase chemical reactants influence the radiative budget of the Earth's atmosphere through scattering and absorption. Detailed simulations of the aerosol size distribution and chemical composition and a comprehensive treatment of emissions and atmospheric chemical reactions are necessary in order to capture the large spatial and temporal variability of trace compounds in the troposphere. Main objectives of the MPI Aerosol, Chemistry and Climate Group are the quantification of the radiative impact of aerosols including all indirect effects, and the quantification of the budgets of reactive gases in the atmosphere including the assessment of climate change impacts. Atmospheric aerosols play an important role by the modification of cloud properties with feedbacks to the hydrological cycle. Furthermore, heterogeneous reactions on the aerosol surface and within liquid aerosol particles interact with the chemistry of the atmosphere. Pollutants condense on aerosol particles so that their transport and deposition are largely determined by the aerosol pathways. Moreover, the deposition of aerosols in the ocean plays an important role in the biogeochemical cycle of the oceans. To increase the understanding of this complex system, the ECHAM5 General Circulation Model (GCM) as part of the Hamburg Earth System Model has been extended by the complex aerosol model HAM and the atmospheric chemistry model MOZART. In the development of the ECHAM5-HAM aerosol model the attempt was made to substantially reduce the number of externally imposed parameters (Stier *et al.*, ACPD, 2004). The aerosol size-distribution, composition, as well as the mixing state are calculated explicitly rendering the explicit calculation of the sink processes and of the aerosol radiative effects possible. The computational efficiency facilitates the usage in long-term climate studies.

Model results are evaluated by comparing to observational data and to other model results within the framework of the model intercomparison project AEROCOM which is jointly organized by the CNRS/Paris (Michael Schulz) and the MPI/Hamburg (Stefan Kinne).

In a series of simulations with this aerosol-climate model, we analyzed the response of the global aerosol system to changes in anthropogenic emissions. In the microphysical aerosol module HAM, sink processes and radiative properties are parameterized in terms of prognosed size-distribution, mixing-state, and composition, establishing degrees of freedom for nonlinear responses of the aerosol system. The analysis of the response of the global aerosol system to the emission changes reveals significant nonlinearities. Global annual-mean mass-burdens respond non-linearly to the induced emission changes, manifested in alterations of the aerosol life-times. For instance, from preindustrial to present day aerosol emissions, the life-time of sulfate decreased by -10.2 %, of black carbon decreased by -22.6 %, for particulate organic matter increased by 10.6 %, and for mineral dust decreased by -1.9 %. The natural sea salt cycle is unaffected by the anthropogenic emissions and shows only negligible variations.

MODES IN M7	SOLUBLE / MIXED		INSOLUBLE
NUCLEATION ($r < 0.005 \mu\text{m}$)	1	N_1, MSO_4	
AITKEN ($0.005 \mu\text{m} < r < 0.05$)	2	$N_2, MSO_4, M_{BC}, M_{OC}$	5 N_5, M_{BC}, M_{OC}
ACCUMULATION ($0.05 \mu\text{m} < r < 0.5$)	3	$N_3, MSO_4, M_{BC}, M_{OC}, M_{SS}, M_{BU}$	6 N_6, M_{BU}
COARSE ($0.5 \mu\text{m} < r$)	4	$N_4, MSO_4, M_{BC}, M_{OC}, M_{SS}, M_{BU}$	7 N_7, M_{BU}

Figure 1: Representation of the aerosol population by seven log-normal modes. For each mode mass and number concentration is predicted.

The impact of specific anthropogenic emission reductions on aerosol cycles with unaltered emissions, manifested in increased life-times, column burdens, and microphysical aging-times, is a clear indicator for the coherence of the aerosol cycles. In a scenario without anthropogenic sulfate emissions, annual global-mean life-times of black carbon, particulate organic matter, and dust increase by 8.9 %, 2.5 %, and 1.5 %, microphysical aging times increase by 164 %, 84 %, and 66 %, and annual zonal-mean column burdens in high northern latitudes increase by up to 70 %, 20 %, and 20 %, respectively. This example emphasizes the need for integrated emission strategies for aerosols and their precursors comprising the cross-connections of the global aerosol cycles.

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The New Thinking relative to the Second Assessment Report

A contribution to ACCENT-T&TP: Chemistry Climate

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The new thinking relative to the Second Assessment Report (SAR) calls for a more flexible and desegregated approach to analysis; it also calls for new forms of interdisciplinarity and more holistic approaches.

TAR emphasises the scientific and policy linkages amongst a number of local (air pollution), regional (acid deposition) and global environmental issues (climate change, stratospheric ozone depletion, loss of biological diversity, desertification, unsustainable forest management, water scarcity and degradation).

Some other phenomena

Most of these changes are on regional rather than global scale, and hence it is more difficult to distinguish and formally attribute them to the global human influence rather than to internal variations, natural forcings or regional human activities.

Urban ozone pollution and the emissions that drive it are important contributors to global climate change. The same pollutants that generate surface ozone (nitrogen oxides, carbon monoxide, and volatile organic compounds) also contribute to the global rise in tropospheric ozone, making it the third most important contributor to radiative forcing after carbon dioxide and methane.

However, the changes observed in the sub-tropical latitudes (Mediterranean) may be the result of increased deforestation. Concerning precipitations in this region:

- globally averaged precipitations are projected to increase; however, at regional scales both increases and decreases are projected. It is obvious that a large uncertainty exists;
- projected climate change will exacerbate water shortage in many water-stressed countries, making unmanaged and poorly managed water systems the most vulnerable;
- extreme events are currently a major source of climate-related impacts and are likely to become more frequent and/or intense under global warming; and
- projected climate change would exacerbate water shortage in many water-stressed countries but alleviate it in some other countries. Climate change is projected to reduce available surface water in many of the water-stressed areas of the world (e.g. in central Asia, southern Africa, and European and African countries around the Mediterranean).

In TAR, the following caveats were mentioned:

- there is little agreement among models concerning future changes in mid-latitude storm intensity, frequency and variability and there is insufficient information on small-scale weather phenomena to make a confident prediction;

- there is a lack of reliable local or regional detail in climate projections for precipitations and for changes in extreme events; and
- there is insufficient information on how small-scale phenomena may change. Very small-scale phenomena such as thunderstorms, tornadoes, hail, and lightning are not simulated in global models.

Feedback processes

Agricultural and ecological systems have many interacting non-linear processes and are thus subject to abrupt changes and threshold effects arising from relatively small changes in the driving variables, such as climate.

Local, regional and global environmental issues are interlinked and affect sustainable development.

Recognizing the linkages among local, regional and global environmental issues, and their relationship to meeting human needs, provides an opportunity to address global environmental issues at the local, national and regional levels in an integrated manner that is cost effective and meets sustainable development objectives.

Human activities, leading to large-scale changes in vegetation cover, are likely to affect regional climate. Changes in land surface characteristics, such as those created by land cover change, modify energy, water and gas fluxes and affect atmospheric composition creating changes in the local/regional climate. In areas without surface water (typically semi-arid or arid), evapo-transpiration and the albedo affect the local hydrological cycle, and thus a reduction in vegetative cover could lead to reduced precipitation at local/regional scale and change the frequency and persistence of droughts.

Our own line of research has been oriented by these ideas, to a large extent because we must provide our politicians with answers to those questions in order to get funded. So far we seem to have evidence that most of these feedbacks work together (simultaneously) in the Mediterranean basin.

Chemistry and Climate Studies at ETHZ

A contribution to ACCENT-T&TP: Chemistry Climate

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The ETH model evaluation global database

The ETH model evaluation global database (ETH-MEG database), formerly known as the "TRADEOFF database", was developed by Dominik Brunner for model evaluation of chemistry transport models (CTMs) and chemistry-climate models (CCMs) within the EU project TRADEOFF (Brunner *et al.*, 2003). The database contains compounds related to photochemistry, its focus is on the UTLS, and it comprises data from the years 1995-1998. It is built upon the "raw" along-flight-path data, averaged over typically 6-min time intervals and merged to a single table per campaign and month. To allow for an easy and direct comparison of numerical simulations with observations, additional "time and position tables" were created by combining the times and locations of all observations of all campaigns available for a specific month. These tables can be used to interpolate at each model time step the simulated tracer concentrations to all observation points available during that time step. In this way model runs can directly be compared to observations taking into account the specific meteorological conditions during each individual measurement campaign.

Within the FP5 project RETRO (see below), the ETH-MEG database will be extended to include historical ozone data. In addition, all available recent data from measurement campaigns, such as TROCCINOX, INCA, or UTOPIHAN_ACT will be added within the framework of the FP6 IP QUANTIFY (start Feb. 2005). Ozone sonde data from the WOUDC archive will be updated, and recent MOZAIC aircraft data will be included. The database is accessible on the web: <http://www.iac.ethz.ch/tradeoff/>.

Within the ACCENT framework, the ETH-MEG database constitutes a valuable tool not only for CTM and CCM evaluation, but also for long-range transport studies and evaluation of chemical-weather models. Note that some measurements such as from MOZAIC might need a special permission to be used.

ETH activities within the EU RETRO project

Investigations on historical ozone changes in the UTLS

RETRO is a project of the EU 5th framework programme. The acronym stands for Reanalysis of the TROpospheric chemical composition over the past 40 years. As the project name indicates, the project aims at investigating tropospheric composition change over the last four decades (1960–2000) using state-of-the-art CTMs that are driven by the ERA40 reanalyses (<http://retro.enes.org>).

Long-term ozone changes in the UTLS of northern midlatitudes

UTLS ozone changes between the second half of the 1970s and the 1990s are investigated using aircraft ozone measurements from the GASP program (NASA, 1975–1979) and from MOZAIC (1994–2003). Ozone climatologies are computed for both periods of time and are then compared to each other to assess changes. First results show that the GASP data reproduce the seasonal cycle in UT and LS ozone properly, as well as the vertical dependence of ozone concentrations. GASP ozone profiles also lie within the uncertainty range of climatological ozone sonde profiles from selected Canadian and European stations.

Evaluation of model sensitivity simulations

Before starting the long-term model integrations, the model performance has been assessed for test simulations of the years 1997–2000 with the models being driven by ERA40 analyses. One part of the evaluation, the comparison of model results to ozone sonde data is being carried out by ETHZ. As an example, Figure 1 shows monthly mean ozone mixing ratios of Goose Bay soundings and the RETRO models (results filtered, with days removed where there is no observation) for the lower, middle, and upper troposphere for the year 1997.

Extension of the ETH-MEG database

Historical ozone datasets such as the GASP program (see above) will be integrated into the database in the course of the RETRO project. The newly incorporated datasets will help to assess the RETRO models' performance in the long-term simulations.

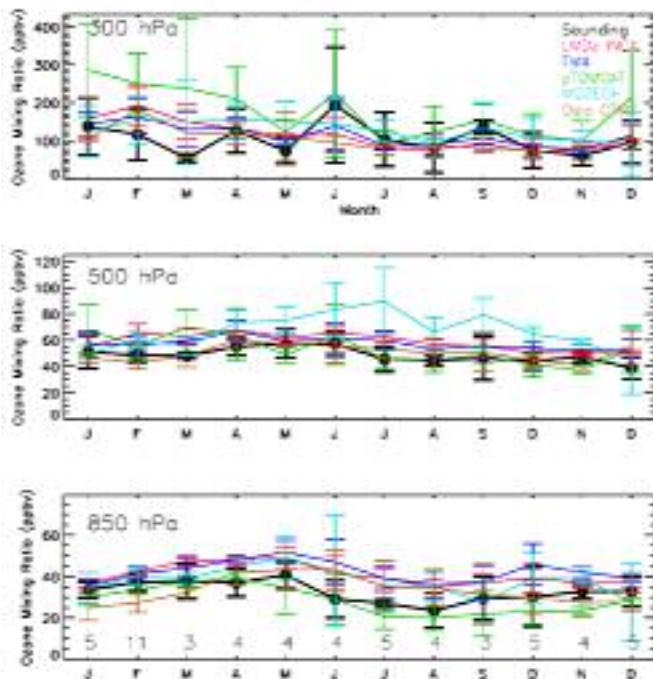


Figure 1: Monthly mean ozone mixing ratios at 850, 500, and 300 hPa at Goose Bay (solid lines) for the year 1997. Vertical bars indicate monthly standard deviations. Numbers in bottom graph (850 hPa) give the number of soundings per month. Models participating in the comparison are LMDzINCA (red), TM4 (blue), pTOMCAT (green), MOZECH (cyan), Oslo CTM2 (brown). Soundings are indicated in black. Note: results not published yet.

Climate sensitivity studies with the SOCOL CCM

SOCOL is a coupled chemistry-climate model that was put together by Eugene Rozanov, who works at the world radiation centre-meteorological observatory Davos (WRC-PMOD). The underlying dynamic model is MA-ECHAM4, which is coupled to the MEZON CTM

(Egorova *et al.*, 2003; 2004). The model's focus is on stratospheric ozone photochemistry, but it also contains tropospheric background chemistry. Thus, in principle, it can also be used to investigate tropospheric ozone effects, such as the influence of stratosphere-troposphere exchange on tropospheric ozone. Currently, several transient simulations of the period 1975-2000 are planned to be carried out to investigate the effects of individual forcing parameters such as greenhouse gases (GHGs), ozone depleting substances (ODS), as well as solar cycle and stratospheric aerosols on the stratospheric composition and circulation. This is done in collaboration with ETH (PhD thesis Martin Schraner). The individual, as well as the combined effects of the forcings will be studied. For example, test simulations of a preliminary model version show an increase in stratospheric water vapour that is of the order of 7-8 %/decade in agreement with the Boulder observations. This result is somewhat surprising since most other coupled chemistry-climate models underestimate the increase in stratospheric water vapour over the last two decades (Austin *et al.*, 2003). The finding will be investigated in more detail in the near future.

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Appendices

A: The Meeting Programme



ACCENT - Transport & Transformation of Pollutants (T&TP)

Frontiers in Transport and Transformation of Pollutants T&TP Barnsdale Discussion Meeting

Programme (to September 2004)

Monday	18th October 2004	
13.00	Lunch and arrival	
14.30	Welcome	Paul Monks
14.40	ACCENT: the project	Michela Maione
15.05	T&TP Barnsdale: the purpose of the meeting	Paul Monks
15.30	Tea	
16.00	Scene Setting: Long-range transport and transformation of pollutants	Isabelle Bey
16.40	Scene Setting: Chemical weather	Hendrick Elbern
17.20	Scene Setting: Chemical complexity	Paul Monks
18.00	Invited Lecture: The Changing Atmosphere: the IGACO Vision for the Future	Peter Borrell
18.30	End of day	
19.15	Mixer and dinner	
Tuesday	19th October 2004	
09.00	Scene Setting: Chemistry and climate	Frank Dentener
09.35	Plenary session: aims of the discussion groups	
	Chemical complexity	Lead: Andreas Volz-Thomas
09.50	Chemical weather	Lead: Øystein Hov
10.05	Chemistry and climate	Lead: John Pyle
10.20	Long Range Transport of Pollutants	Lead: Kathy Law
10.35	Coffee	
11.00 – 12.30	Discussion groups – Session 1	
12.30 lunch		

14.00 – 18.00	Discussion groups – Session 2	
19.00	Dinner	
Wednesday	20th October 2004	
09.00	Invited perspective: Transport and Chemical Problems in the Mediterranean	Millán Millán
09.35	Invited perspective: Urban Scale Processes	Nicolas Moussiopoulos
10.10	Coffee	
10.30 – 12.30	Discussion groups – Session 3	
12.30	Lunch	
13.30	Free for <ul style="list-style-type: none"> ○ using the Barnsdale facilities; ○ outside activities or private meetings; ○ leaders and rapporteurs to prepare presentations 	
19.00	Conference dinner	
Thursday	21st October 2004	
09.00	Plenary session; reports from the task groups	
	Chemical complexity	Jonathan Williams
09.30	Chemical weather	Mark Lawrence
10.00	Chemistry and climate	Martin Schultz
10.30	Coffee	
11.00	Long-range transport of pollutants	Claire Reeves
11.30	Tasks for the future; what have we learned?	Paul Monks
12.45	Conclusion	
13.00	Lunch and departure	

B: The participants

1. Chemical Complexity		-
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3. Chemical Weather		-
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4. Chemistry and Climate		-
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C: Briefing Sheet for Participants

Frontiers in Transport and Transformation of Pollutants ACCENT T&TP Barnsdale Expert Discussion Meeting

Briefing Sheet

Aim

The aim of the meeting is to explore the main issues and directions in atmospheric chemical oxidation and transport, and to lay the basis for future cooperative work and a set of authoritative reviews in each of the fields.

Organisation

The meeting will be organised around guided discussions on four topics with a leader and rapporteur for each discussion group.

<i>Topic</i>	<i>Leader</i>	<i>Rapporteur</i>
<i>Chemical complexity</i>	Andreas Volz-Thomas	Jonathan Williams
<i>Long-range transport</i>	Kathy Law	Claire Reeves
<i>Chemical weather</i>	Øystein Hov	Mark Lawrence
<i>Chemistry/climate interactions</i>	John Pyle	Maria Kanakidou

There will be several plenary and scene setting lectures and a plenary discussion on future directions, both for the scientific field and for the T&TP project.

Contributions

All participants will be expected to contribute to the discussions with voxboxes, *i.e.* brief contributions of key scientific points, results or conclusions, illustrated with one or two overheads.

- ★ You should contact your group leader before the meeting to let him/her know how many contributions you would like to make. How many voxbox contributions a participant will make will be at the discretion of the group leader.
- ★ Participants will also be expected to produce, at the meeting or before, an electronic version of a brief one or two page summary of their contributions to T&TP, and to provide their voxbox contributions in an electronic form complete with illustrations.

The aims of the individual groups.

It is hoped that the outcome of the meeting will be a set of four review articles to be published in the literature on the group focus topics. These should review the current state of each field, highlight and elaborate the scientific problems and outline the future directions the field is likely to take. An additional section on the realistic policy applications and environmental impact would be most valuable.

At the end of the meeting each group should have produced

- (a) material for a presentation at the plenary session on the results from the group;
- (b) a 4/5 page summary of the main points emerging from the discussions;
- (c) the names of the team who will write the sections and edit the articles; and in addition,
- (d) a list of suggestions for future, timely, T&TP expert discussions.

Paul Monks; T&TP Coordinator
Peter Borrell, Deputy

D: Briefing Sheet for Session Chairs and Rapporteurs

Session Chairs and Rapporteur Briefing Sheet

Aim of each Group

It is intended that the outcome of the meeting will be a set of four review articles to be published in the literature on the group focus topics. These should review the current state of each field, highlight and elaborate the scientific problems and outline the future directions the field is likely to take. An additional section on the realistic policy applications and environmental impact would be most valuable.

At the end of the meeting each group should produce:

- (a) material for a presentation at the plenary session on the results from the group;
- (b) a 4/5 page summary of the main points emerging from the discussions, suitable for publication in the meeting report;
- (c) the names of the team who will write the sections and edit the articles; and in addition,
- (d) a list of suggestions for future, timely, T&TP expert discussions.

Structuring the discussion sessions

There are three major discussion sessions for each group. It is envisaged that the rapporteurs and leaders will want to use Wednesday afternoon to put together the summary presentations for Thursday.

Participants, in their briefing sheet, have been invited to bring a few salient overheads to the meeting to illustrate key discussion points in the form of voxboxes, and to contact you about them.

- ★ In order to structure the discussion sessions it would be prudent to contact the group members, *before the meeting*, to raise or to talk about specific issues, and control the number of voxboxes offered. The use of these sub-topics may be quite important; you could choose several and ask participants to speak to these.

Some potential discussion points

Here are a number of suggested questions, *some* of which you may want to adopt. "XXXX" refers to your group. Please remember that the key focus should be on the science; the wish is to stimulate discussion on the scientific aspects of the problem.

- a) What do we understand/ what is the scope of the proposed discussion? (*i.e.* what is XXXX?)
- b) What have been the major scientific findings in XXXX?
 - a. Historically
 - b. What are the ten most important papers in XXXX (in last 10 years)?
 - c. What are the current hot topics in XXXX?
- c) What is the current scientific understanding/state of the art for XXXX?
 - a. What role do models/measurements/observations play in XXXX?
 - b. How can we break down XXXX into sub-parts?
- d) In what ways are we limiting ourselves with respect to XXXX?
- e) What is the requirement for a multidisciplinary understanding of this problem?
- f) How important is XXXX in the atmospheric context?
- g) What are the key feedbacks into policy from XXXX?
- h) What are the missing science gaps in XXXX?
- i) What new experiments/observations are required to understand XXXX? Which of these are most pressing? What is the requirement for the development of new techniques?
- j) What is the future direction for XXXX?
- k) What can ACCENT do to fulfil future requirements?

Suggestions for Future Meetings

We would be grateful if groups could come up with one or more topics for future T&TP Expert Meetings. The topic should be timely in the sense that it is appropriate to try to draw the field together, and also perhaps that it is a good time to identify new avenues to explore

Paul Monks; T&TP Coordinator, Peter Borrell, Deputy.

E: The Invitation**ACCENT-Transport & Transformation of Pollutants (T&TP)**

Address

Dear XXX,

**Frontiers in Transport and Transformation of Pollutants
T&TP Barnsdale Discussion Meeting***Invitation*

Paul Monks has asked me to write to you on behalf of the ACCENT T&TP Theme Steering Group, to invite you to the first meeting of the group to be held at the

Barnsdale Hall Hotel, Rutland Water, UK

from Monday 18th October 2004 to Thursday 21st October 2004.

We would like you to participate in and contribute to the discussions of the Chemical Weather Group. We would be prepared to pay your travel expenses to attend the meeting.

Aim

The aim of the meeting is to explore the main issues and directions in atmospheric chemical oxidation and transport, and to lay the basis for future cooperative work and a set of authoritative reviews in each of the fields.

Organisation

The meeting, attendance at which is by invitation only, will be organised around guided discussions on four topics: Chemical complexity, Chemical weather, Chemistry/climate interactions, and Long Range Transport. A number of distinguished colleagues are being asked to act as Discussion leaders and Rapporteurs, and the final combined session will be devoted to reports from each of the Groups and a general discussion on future directions, both for the scientific field and for T&TP.

Contributions

All invited participants will be expected to contribute to the discussions with voxboxes, *i.e.* brief contributions of key points, results or conclusions, illustrated with one or two overheads. Participants will also be expected to produce, at the meeting, a brief one or two page summary of their contributions to T&TP in a prescribed format.

Travel Expenses

The Committee of T&TP will be prepared to pay the necessary travel expenses of the invitees and to accommodate them at the Barnsdale Hall Hotel. In order to receive travel support, it will be necessary to observe the booking conditions, and to produce the required abstracts at the meeting.

Venue

Paul has chosen a lovely venue for the first meeting (<http://www.barnsdalehotel.co.uk/>) and we do hope that all the major European members of this important field will attend.

Reservation

If, as we hope, you wish to accept this invitation, kindly let us know (pborrell@luna.co.uk; P.S.Monks@leicester.ac.uk) by return please.

We do look forward to seeing you at Barnsdale.

With best wishes,

Peter Borrell (*on behalf of Paul Monks and the T&TP Steering Committee*).