Transport and Transformation of Pollutants (T&TP)
Access to Emission Data, Access to Laboratory Data,
Aerosols, Remote Sensing from Space (AT2),
BIAFLUX, Modelling

AT2

BIAFLUX

10 Contributions from the Group 1 Participants

Investigating changes in photo-oxidants, precursors and feedback mechanisms, with changing temperature and land use

Aggregation of CO_2 Fluxes over Land

A contribution to ACCENT CCAQ: Group 1

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Summary

A budget method to derive the aggregated (regional) surface flux of CO_2 over a patchy landscape from the evolution of the boundary layer is applied. The necessary input for the method can be deduced from a combination of vertical profile measurements of CO_2 concentrations by *i.e.* an airplane, successive radio-soundings and standard measurements of the CO_2 concentration near the ground. The method is used to derive aggregated flux of CO_2 over a site at Zealand in Denmark during an experiment 12th–13th June 2006. The aggregated fluxes of CO_2 represent a combination of agricultural and forest surface conditions. It was found that the aggregated flux of CO_2 in broad terms follows the behavior of the flux of CO_2 at the agricultural (wheat) and the deciduous forest station. The aggregated flux is comparable not only in size but also in the diurnal (daytime) cycle of CO_2 fluxes at the two stations. It is interesting to note that the vertical extent of the boundary layer and the residual layer are easily recognized from vertical profiles of CO_2 concentration performed by the airplane.

Introduction

Neither the land nor the sea surface can be considered homogeneous with respect to fluxes of CO_2. The aggregation of CO_2 fluxes to land surfaces is a critical factor when setting up the budget of the sources and sinks of carbon as done in the context of climate research and integrated assessment models for the environmental status. In climate models, the individual horizontal grid cells often enclose regions of pronounced patchiness in the vegetation. The formation of the aggregated fluxes depends in a non-linear way on the patchiness of the landscape. Although the effect of the non-linearity is poorly explored the estimation of the spatially integrated fluxes is central for a large number of scientific, practical and even political assessments of the role of CO_2 emissions for our present and future climate and environment.

Mass balance for CO_2, measurements

Here the aggregated flux of CO_2 is derived from a mass budget for CO_2 extending from the surface to the top of the atmospheric boundary layer, thus taking into account the patchiness of the landscape. The meteorological conditions during the experiment were typical for a well developed large scale high pressure system, low wind speed from varying directions, a cloud free sky and strong insolation resulting in flux around noon of $\approx 200\ Wm^{-2}$ for the sensible heat and exceeding $300\ Wm^{-2}$ for the latent heat. In the afternoon the temperature went beyond 25 °C. Such conditions give rise to a considerable growth of the boundary layer and are characterized by negligible advection. They are thus very favorable for the use of the budget method.

Micrometeorological measurements including fluxes and concentration of CO_2 were carried out over an agricultural site near Risø (RIMI) and over a beech forest in the centre of Zealand (Lille Bøgeskov); both monitoring stations are part of the

CarboEurope network, Figure 1. During an intensive measuring campaign 12th–13th June 2006 the measurements were extended with profiles of CO_2 by a research airplane. The height of the boundary layer as function of time was determined experimentally by releasing radio sondes at intervals of 3 hours at 06, 09, 12, 15 and 18 local time (= GMT + 2).

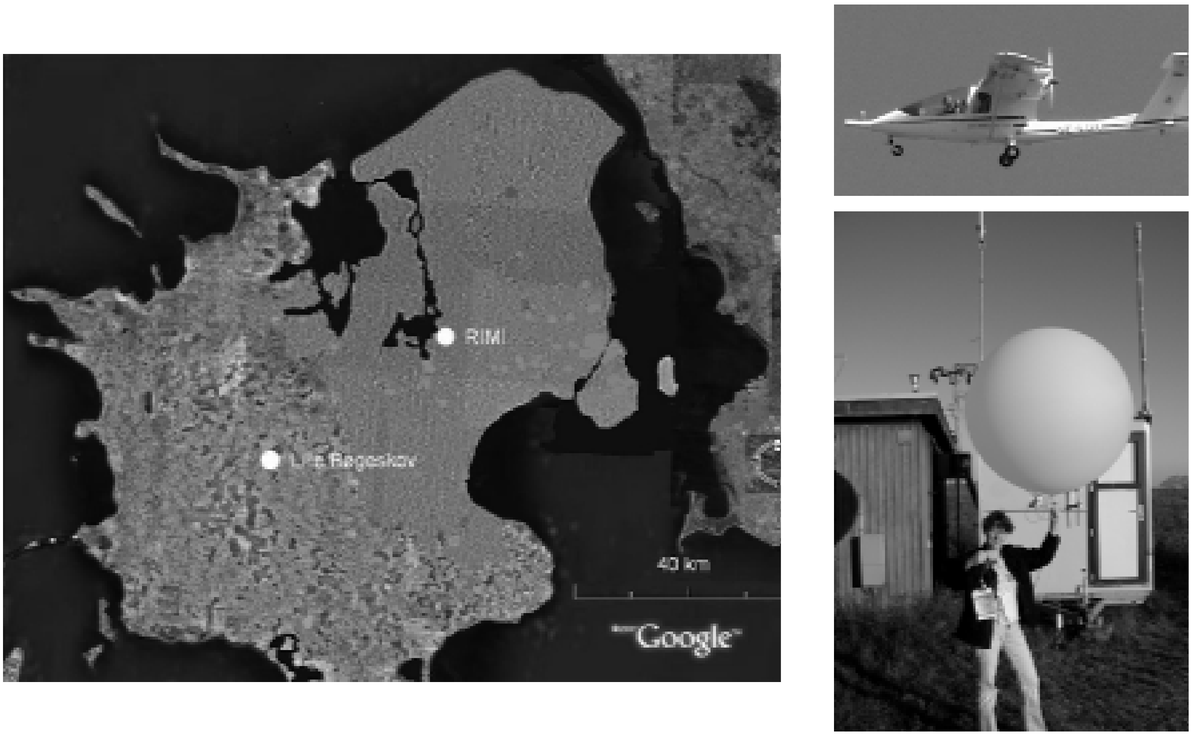

Figure 1. Left panel: The position of the two measuring sites on the island of Zealand, Denmark; RIMI (agricultural) and Lille Bøgeskov (deciduous forest). Right panels: Pictures from the RIMI site during the experiment; the aircraft and a launch of a radio sonde.

Analysis

To derive the aggregated flux of CO_2 to the surface from the mass balance method the development of the boundary layer, as well as the concentration of CO_2 above the boundary, and the concentration of CO_2 near the ground should be known as function of time. The height of the boundary layer was determined from successive the radio soundings. Interpolation of the height of the boundary layer was performed by use of a formula suggested by Batchvarova and Gryning [1991]. The height of the atmospheric boundary layer can also been detected in the vertical profiles of the CO_2 concentrations that were measured by the airplane, Figure 2. On both days it can be seen that the CO_2 concentration inside the boundary layer is about 365 ppm and approximately constant with height. On 12th June a jump of 5 ppm in the CO_2 concentration at 500 meters height marks the top of the growing boundary layer. On 13th June a jump in the CO_2 concentration at 1000 meters indicates the top of the boundary layer. It can be seen that the next jump takes place at about 1700 m which marks the top of the residual layer (top of boundary layer from the foregoing day). Above the residual layer the CO_2 concentration is about 380 ppm. The smaller concentration inside the boundary layer is caused by uptake of CO_2 by the vegetation. The boundary layer heights on both days are in agreement with the estimate from the radio sonde measurements.

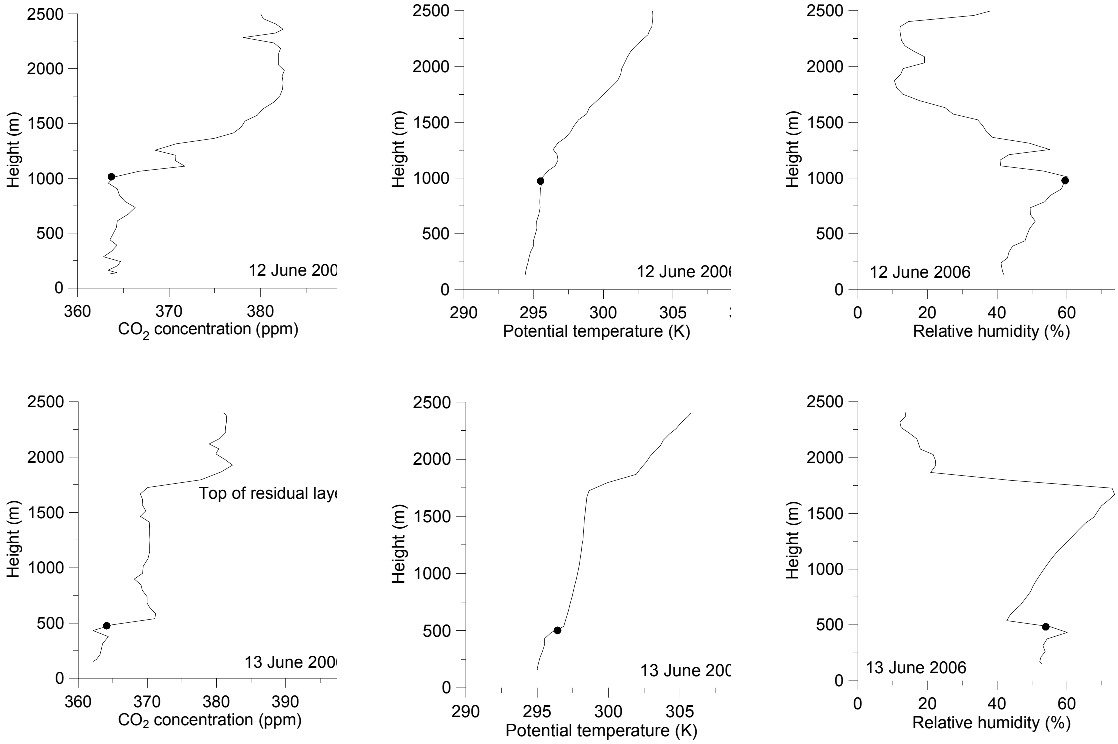

Figure 2. Profiles measured by the aircraft near the RIMI site of CO_2 concentration, potential temperature and relative humidity. The upper panels shown are from 12th June at around 09:50 GMT. The height of the boundary layer is estimated to be 1000 m, it is indicated by the full circle. The lower panels are for 13th June around 08:40 GMT. Here the height of the boundary is estimated to be 500 meters.

Aggeregated CO_2 fluxes

Using the above parameters the aggregated fluxes were determined by the budget method [Gryning *et al.,* 2001], Figure 3.

It can be seen that the aggregated flux of CO_2 in broad terms follow the behavior of the flux of CO_2 measured at RIMI (wheat) and Lille Bøgeskov (deciduous forest). It is promising to see that the aggregated flux is comparable not only in size but also in the general diurnal (daytime) cycle of CO_2 fluxes at RIMI and Lille Bøgeskov. It can be seen from Figure 3 and Table 1 that during daytime the integrated downward CO_2 flux over the beech forest is larger than over grassland indicating the important role of forest as a carbon sink.

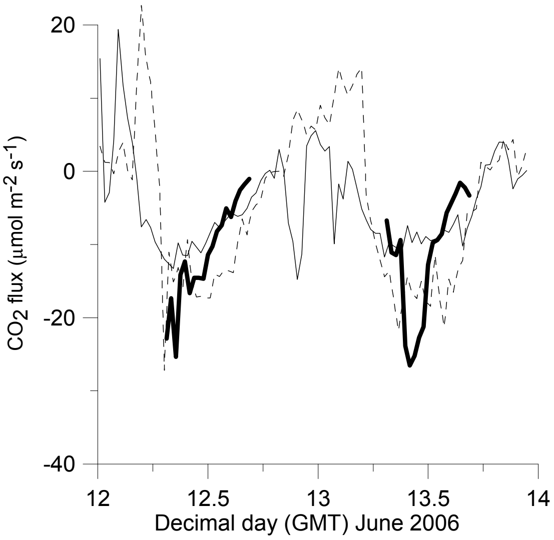

Figure 3. Measured CO_2 fluxes near the surface at RIMI/wheat (thin solid line), Lille Bøgeskov/deciduous forest, (thin dashed line), and the regional CO_2 fluxes from the boundary layer method (thick solid line).

Table 1. Averaged fluxes of CO_2

	Fluxes of CO_2 (μmol m^{-2} s^{-1})		
Period 7:00 to 16:30 GMT	Aggregated RIMI regional	RIMI agricultural wheat point	Lille Bøgeskov deciduous forest point
12th June 2006	−11.1	−8.9	−14.2
13th June 2006	−11.5	−9.1	−15.6

Discussion

The required information for use of the boundary layer method is: 1) measurements on the concentration of CO_2 at the surface, 2) vertical profiles of CO_2 concentration in order to estimate the jump in concentration at the top of the boundary layer, 3) information on the growth of the boundary layer.

The jump of the CO_2 concentration at the top of the atmospheric boundary layer can be measured by airplanes, but this is extremely costly. The development of a CO_2 sensor that can be attached to a radio sonde and sensitive enough to measure the structure of the CO_2 profile would constitute a major scientific breakthrough for research in CO_2 aggregation.

The method is applicable at meteorological conditions such that the boundary layer is well developed and advection is negligible These condition are typical for a large scale high pressure systems, where the heat fluxes are usually high resulting in a rapid growth of the boundary layer and a well defined top, the wind speeds are low from varying directions and consequently advection is generally negligible.

Models (NWP and MMM) predict poorly the boundary-layer height and sensible and latent heat fluxes to the ground.

The interplay between the height of the boundary layer and the non-linear aggregation of surface fluxes over patchy landscape is important but poorly accounted for in CC and MMM models.

The aggregation issue is a very important issue for climate change because land use change will take place on all scales.

Conclusions in relation to CC and AQ modelling

The NWP or MMM used for weather prediction, air quality forecasts are predicting well temperature, wind, precipitation to some degree, while parameters as PBL height, momentum and heat (sensible and latent) fluxes at the surface are poorly predicted. In the same time the processes of exchange of energy and compounds between the atmosphere and the surface are key issues in air pollution and climate modeling. Thus basic research on exchange processes, vertical profiles and horizontal aggregation of fluxes is still needed in order to improve the boundary layer parameterizations in all models.

Acknowledgements

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Laboratory Kinetics Data for Climate−Atmospheric Chemistry Interactions – Some New Challenges for Data Evaluation

A contribution to ACCENT CCAQ: Group 1

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Chemistry data for modelling climate impacts

Investigation of Chemistry-Climate interactions requires chemical schemes in predictive models. Explicit chemical mechanisms with elementary reactions have been used for some time to build predictive chemical models for photo-oxidant formation. More recently the chemistry leading to precursors and mechanisms for secondary organic aerosol (SOA) formation has been a subject of attention. These models have need for chemical kinetics data, which requires a vital knowledge transfer link between kineticists and climate scientists.

Key climate change parameters which influence chemistry (*i.e.* rate constants, chemical pathways, photolysis constants) are: Temperature, Humidity and composition changes driven by surface exchange and heterogeneous chemistry. In a warmer world it is expected that emissions of biogenic VOCs will be augmented, leading to increased complexity of the degradation mechanisms. This leads to new free radicals and SOA precursors.

Over the past few years a project has been undertaken to enhance the accessibility and availability of the evaluated kinetic data base, which has been assembled by the IUPAC Subcommittee for Gas Kinetic Data Evaluation for Atmospheric Chemistry, by placing the material in a database on an interactive site on the www. The creation of the website (http://www.iupac-kinetic.ch.cam.ac.uk/) has been implemented with support from IUPAC Division of Physical Chemistry, and from the EU project 'Network Of Excellence on Atmospheric Composition Change', ACCENT. The Subcommittee has continued to expand and update the evaluations, which have been also been published in a series of four peer reviewed articles in *Atm. Chem. Phys.*[Atkinson *et al,* 2004, 2006, 2007, 2007a] Some key issues arising in these updates and expansions are flagged up below.

Temperature dependence of gas-phase OH reactions

The temperature dependence of rate constants for simple bimolecular reactions is generally represented by the Arrhenius expression. However this is often adequate only over limited temperature range and accurate representation of the experimental data over wider T range requires a modified expression of the form AT^n exp(-E/RT). For example experimental data for the reaction:

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

are in good agreement. However the Arrhenius expression underestimated the rate coefficient at the mean atmospheric temperature of 278 K. The currently recommended expression using shows slight curvature over the range 195−425 K leading to a slightly lower rate coefficient and a consequent 20 % upward revision of the mean lifetime of atmospheric methane.

Much greater non linearity is apparent in the rate expression for the reactions involving oxygenated volatile organic species, for example,

$$OH + CH_3C(O)CH_3 = CH_3C(O)CH_2 + H_2O$$

which is best represented by a bi-exponential expression giving a much faster rate at low temperatures.

Complex P, T and H_2O dependences in peroxy radical reactions

Bimolecular reactions proceeding via complex intermediates have complex rate expressions. There are many examples but no general formula applies. An important example of this type of reaction is the reaction of peroxy radicals with NO. A minor channel in the RO_2 + NO reaction (R = organic group with > 4 C atoms) is the formation of $RONO_2$ is well established. The branching ratio increases with C number, with decreasing T and with increasing pressure but experimental data only covers a limited number of RO_2. In view of the critical importance of this reaction in the partitioning of NOx in the troposphere a Structure Activity Relationship (SAR) needed to define the rate parameters. So far an RRKM treatment of isomerisation of the ROONO intermediate fails and a better understanding of the mechanism of this type of reaction is needed.

H_2O dependence of HO_2reactions

Formation of $HONO_2$ from HO_2 + NO has been determined in a single experimental study and also shows complex pressure, temperature and water vapour dependence [Le Bras *et al,* 2006]. These results have a quite profound influence on ozone production and NOx budgets in the troposphere and require confirmation. Other reactions of HO_2, for example with organic peroxy radicals to form hydroperoxides, may also be influenced by pressure and H_2O, and the kinetics of processes these remain to be carefully measured. Need for new experimental studies in critical areas is hindered by lack of funding for this aspect of atmospheric chemistry, which has resulted in a diminished active scientific effort in this area.

Complexity of VOC degradation

Investigation of Chemistry-climate interactions and feedbacks presents a new dimension to the atmospheric chemistry of biogenic and anthropogenic VOC through their impact on oxidation capacity and secondary organic aerosol formation. New challenges are presented through the complexity in degradation mechanisms of VOC. The introduction of reactions for isoprene degradation into the IUPAC data base introduced 17 new reactions just to descrobe the formation of first generation products. There are common patterns in degradation mechanisms, but the detailed structure dependence of rate coefficients are required, especially those for critical T-dependent reactions which influence degradation pathways and products, *e.g.* alkoxy radical isomerisation /decomposition. Structure–reactivity relationships offer a promising approach to address this complexity. For example [Atkinson, 2007b] has used experimental and theoretical data to investigate SARs for alkoxy radicals.

Mechanism development MCM

There is a need for kineticists to formulate and update mechanisms/schemes for atmospheric chemistry models, using evaluated data from experiments and SARs. An attempt is being made to link the Master Chemical Mechanism to the evaluated IUPAC database via automatic IT-based links, enabling better knowledge transfer between the kinetics and modeling expertise. This is being supported by ACCENT and a new NERC KT project.

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Climate Change and Air Quality for Baltimore and Washington

A contribution to ACCENT CCAQ: Group 1

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Summary

The atmospheric chemistry group at the University of Maryland has been conducting research on air pollution over the Baltimore/Washington area for 15 years – a period long enough to determine inter-annual variability and isolate the impacts of changes in emissions from changes in weather.

Introduction

Although considerable progress has been made over the past few decades, the Mid-Atlantic region of the eastern US, a heavily populated region home to both Baltimore and Washington, DC, suffers from photochemical or Los Angeles-type smog as well as heavy loadings of particulate matter. These problems peak in the warmest months of the year, and global climate models [IPCC, 2001, 2007] predict warmer summers for this region. Although how these higher average temperatures will manifest themselves remains uncertain, it is possible that longer or more frequent heat waves could erase the progress made by reducing pollutant emissions. Here we investigate the relationship between temperature and pollution levels as well as the trend in regional meteorology as indicated by movement in the position of the jet stream. Finally we examine changes in local land use as a possible method for alleviating these effects.

Mickley *et al.* [2004] reported that global warming will decrease the occurrence of cyclonic waves and associated fronts. This could lengthen the duration of stagnant, high pressure events (such as the Bermuda High with hot and hazy weather) and delay the onset of cold fronts that clean up air pollution episodes. Hogrefe*, et al.*, [2004] used a global climate model and a mesoscale weather model to drive a chemical transport model; they found increases of 3-5 ppb in 8-hr average ozone over the eastern US before the end of this century, due primarily to changes in regional climate. Researchers at Cambridge [Pyle*, et al.*, 2007] ran the UK Meteorology Office global model and found even greater increases in ozone, 10-20 ppb over the eastern US by the year 2100. In contrast, Tagaris *et al.* [2007] simulated summer and annual mean ozone and particulate matter (PM) using the EPA-approved CMAQ model driven by a NASA climate model. They found that for local air quality the impact of global climate change was small compared to the impact of regional emissions controls. Assuming major reductions (> 50 %) in releases of SO_2 and NOx over North America, they estimate decreases in ozone of 11-28 % and decreases in PM of 9-32 % by 2051. Other modelling studies [Dawson *et al.*, 2007] suggest that $PM_{2.5}$ will decreases in concentration with increasing temperatures, due to dissociation of ammonium nitrate. Here we examine ambient data to evaluate this prediction.

The climate of the mid Atlantic region is being altered by changes in the composition of the global atmosphere (such as greenhouse gases) and the local atmosphere (such as aerosols) as well as in local land use. Baltimore and Washington should be in compliance with the National Ambient Air Quality Standards (NAAQS) by 2009, but changes in the global background pollutant levels and in local weather could reverse this progress.

Scientific activities

Research at UMD has demonstrated a marked increase in ozone (photochemical smog) and haze with increasing temperature (Figures 1 to 3).

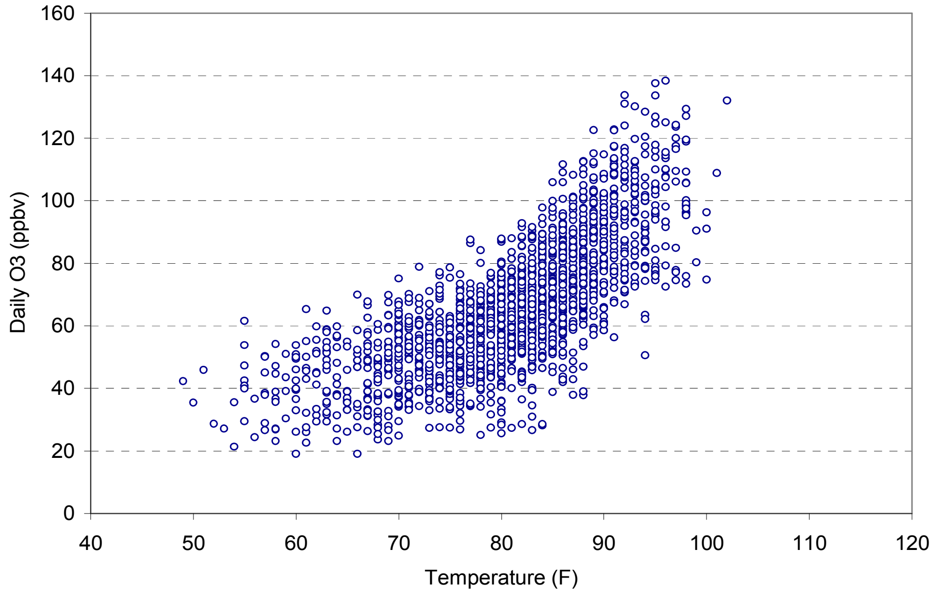

Figure 1. The response of ozone to temperature for the warm months in Maryland. Maximum surface temperature at BWI versus peak 8-hour ozone concentrations in the Baltimore non-attainment area for the period May to September 1994 to 2004 [Piety, 2007]

The current state of the science indicated that without further reductions in pollution emissions, the hotter weather will almost certainly mean worse air quality for Maryland and environs. The decreased frequency of cold fronts and increased frequency of heat waves are conducive to smog episodes. Historically, ozone has increased by about 2 ppb K^{-1}. Figure 2 shows how use of a conditional mean for the grand ensemble of available data can bring out the impact of emissions reductions despite the vagaries of the weather.

High smog events occur when the Subtropical Jet Stream is within 200 km of Baltimore. Examination of the TOMS ozone column content [Hudson *et al.*, 2003, 2006] has shown northward advancement of the position of this Jet Stream (Figure 4). Along with an increase in average temperature, the frequency of days that the subtropical jet was within ~200 km of Baltimore has increased by about 50 % between 1979 and 2003.

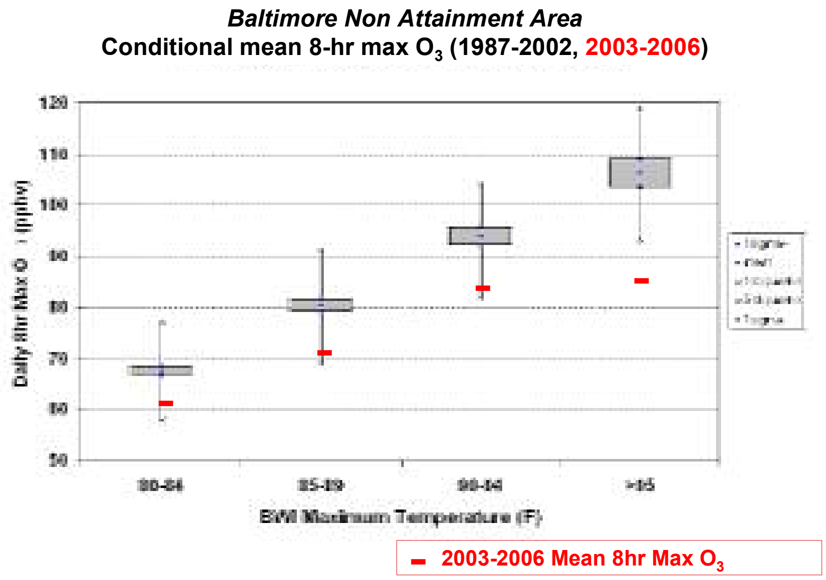

Figure 2. Demonstration of the success of the NOx emissions reduction associated with the SIP Call. Prior to the decrease in emissions (large grey boxes), ozone was higher in all temperature categories. After power plants were cleaned up in 2003 and 2004 (small red marks), ozone was reduced substantially.

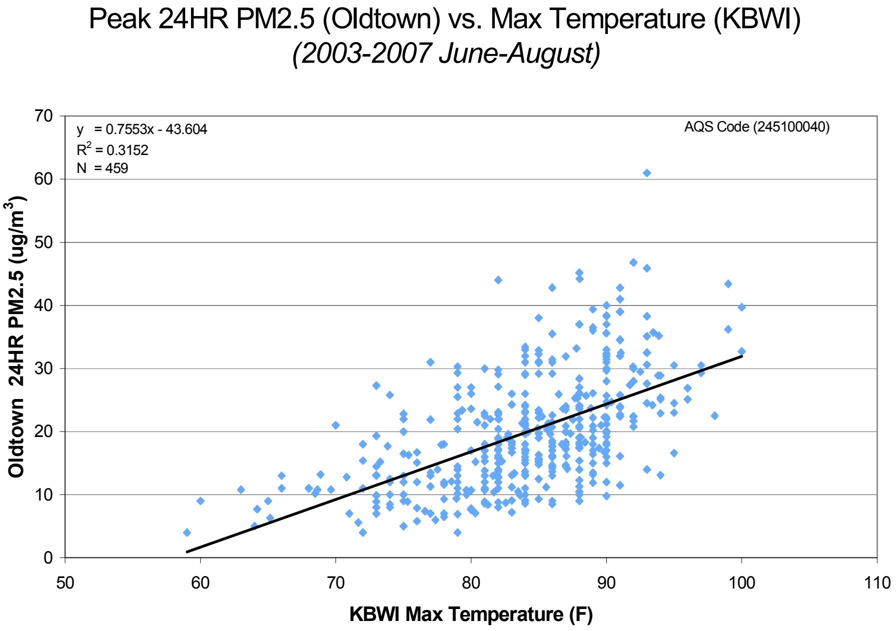

Figure 3. The trend in PM in Baltimore as a function of local maximum temperature. The slope is greatest at highest temperatures, but positive in all seasons.

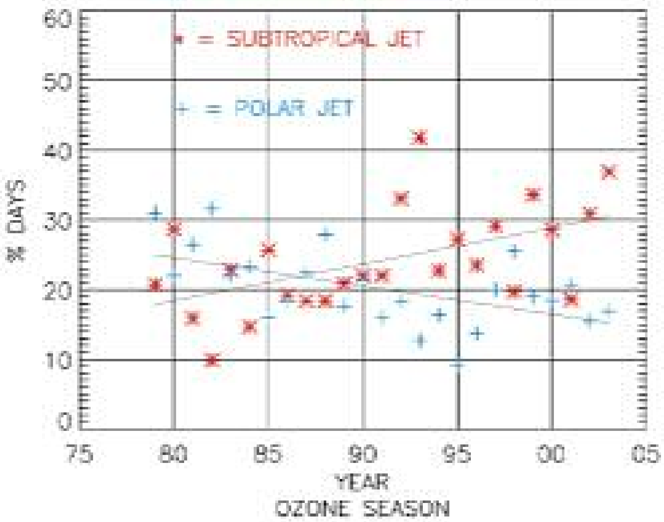

Figure 4. Percent of days when jet stream within 200 km of Baltimore.

Loss of visual range and increased morbidity and mortality due to higher concentrations of fine particulate matter are likewise probable. The mechanism for these impacts involves persistent anticyclones that lead to weak or stagnant winds, high daytime temperatures, and intense UV radiation reaching the Earth's surface. Weak winds allow pollutants to build up; high temperatures increase the evaporation of volatile organic compounds (VOCs) from fossil fuels such as gasoline vapor that acts as a precursor to PM and ozone. Increased temperatures from the urban heat island effect [Jin *et al.*, 2005; Kalnay and Cai, 2003] are well documented and could exacerbate these effects.

Historically, urban PM loading also increased with increasing temperature. For the summer months (June, July and August) the slope is 1.4 µg m^{-3} K^{-1} for all days, and climbs to 1.6 µg m^{-3} K^{-1} for the hottest days. In winter, the slope is 0.4 µg m^{-3} K^{-1}, but r^2 is still significant at 0.18; this contrasts sharply with the CMAQ model predictions.

Certain trees emit biogenic VOCs such as terpenes from pines, µ and isoprene from oaks. These compounds react with man-made pollutants to generate smog and haze. Higher temperatures and higher CO_2 concentrations accelerate emissions. Changing climate, in addition, is predicted to cause shifts in climax ecosystems [Iverson and Prasad, 2002; McKenney-Easterling *et al.*, 2000] with a trend away from maple/beech toward oak/pine forests with higher emissions of VOCs (Figure 5).

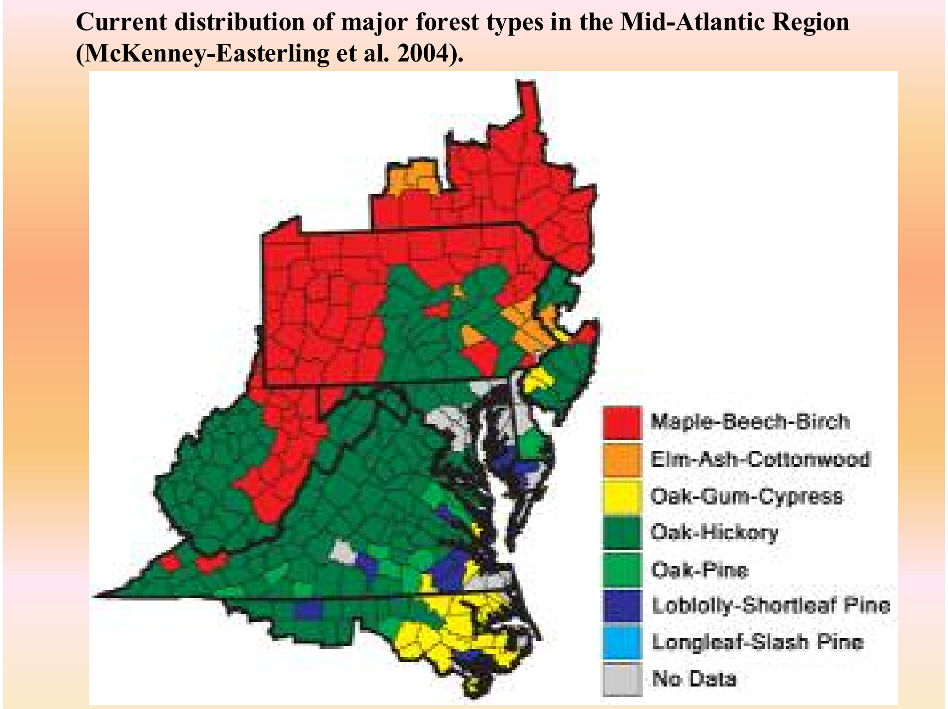

Figure 5a. The distribution of major tree types with current climate conditions. Maples are low isoprene emitters; oaks are high emitters.

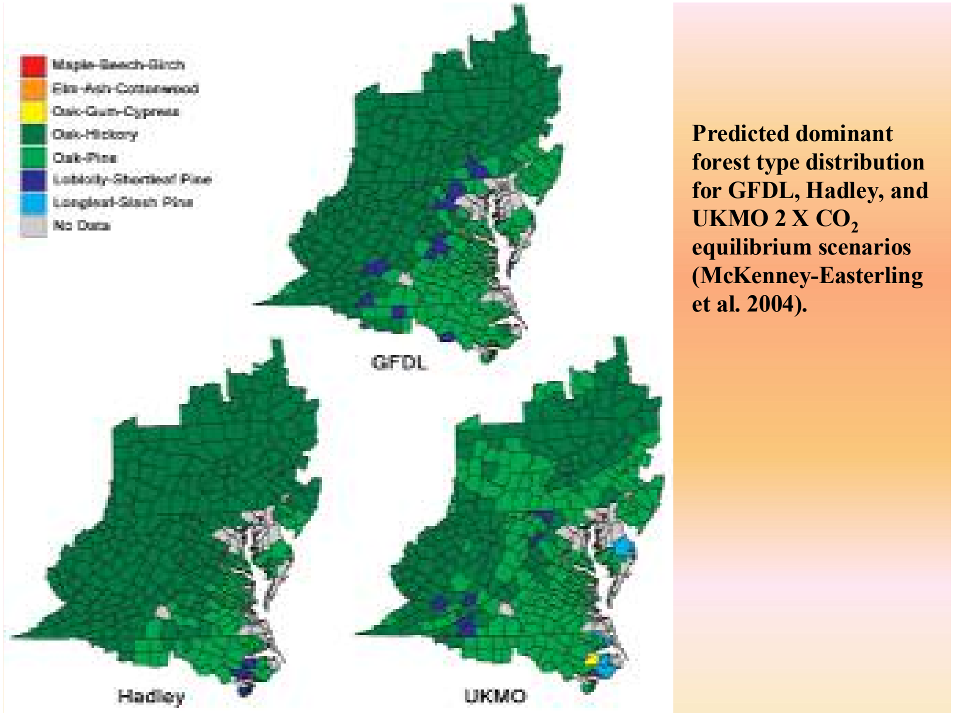

Figure 5b. The distribution of major tree types under several possible future climate predictions.

Future outlook

Planned work at UMD will include numerical simulation with the WRF weather model and CMAQ air pollution model, and investigation of trends with satellite data. We are currently investigating the potential impact of land use, specifically increasing tree cover, on weather and air quality in the mid Atlantic region. In numerical simulations with all urban areas replaced with forests, benefits in the form of cooler temperatures are predicted – these should lead to reduced ozone and PM. Similar specialized investigations could be conducted into the impact of global warming on Maryland's air pollution and its effects on water quality, as well as the health of Maryland's citizens and environment.

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Assessing the Future Impacts of Biogenic VOC Emissions on Air Quality

A contribution to the ACCENT CCAQ: Group 1

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Depending on location and environment biogenic volatile organic compounds (BVOC) can make important contributions to the generation of photochemical smog and in particular the formation of ozone and fine particles. The interaction of natural emissions with anthropogenic NOx to form ozone has been established for many decades and is already seen as a key challenge in air pollution abatement. The role of BVOC in the formation and modification of particles is a less mature field and one where the exact mechanisms, both chemical and physical, are still being explored. The primary biogenic emission from vegetation globally by mass is isoprene and the emission of this compound to the atmosphere has been the subject of extensive study. Empirical predictive formulae exist that can mimic observations and for isoprene, the emission strength is known to be a function of increasing solar radiation and temperature, up to some maximum value around 40 °C before diminishing. The strong coupling between isoprene and temperature gives this species extra importance in regions of high temperatures, and in Europe it can become a dominant VOC during synoptic scale air pollution episodes associated with summertime high pressure systems. Figure 1 below shows a typical relationship between observed ambient isoprene and 10 m air temperature measured in south eastern England during summer 2003.

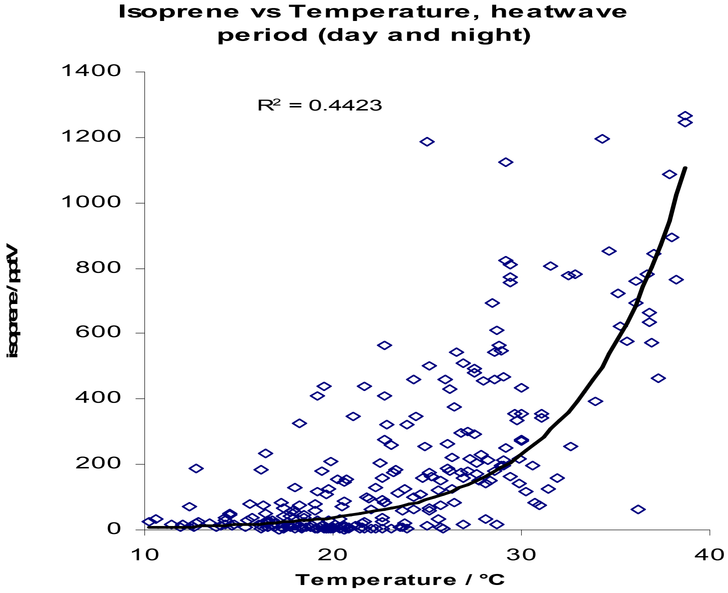

Figure 1. Hourly observations of ambient isoprene and 10 m air temperature measured in south eastern England during summer 2003.

Under typical U.K. summertime conditions where air temperatures are around 24 °C, isoprene is rarely seen to exceed 400 parts per trillion. Under heat wave conditions however ambient isoprene concentrations can frequently exceed 1000 pptV and its influence on ozone formation grows proportionally [Lee *et al.,* 2006]. The temperature coupling of isoprene in combination with meteorological predictions of a greater frequency in severe summertime heat wave conditions leads to a natural chemistry-climate linkage between isoprene and air quality in the future. This attractive and relatively simple relationship is complicated somewhat by conflicting and poorly understood factors associated with for exampling plant response to increasing CO_2 and decrease in water availability.

Whilst isoprene has received the majority of attention as an emission that may affect future air quality, it is not the only reactive BVOC emission with impacts on photooxidants. Monoterpene emissions can make up an important fraction of biogenic emissions from vegetation but our knowledge of these species and their future climate response is less good than for isoprene. Much of the uncertainty surrounding monoterpenes lies in their speciation and individual reaction pathways. Figure 2 below shows a typical GC-MS analysis of air from a biogenic influenced environment and illustrates that whilst isoprene is an important component of the biogenic sourced mixture many other natural emissions are also present.

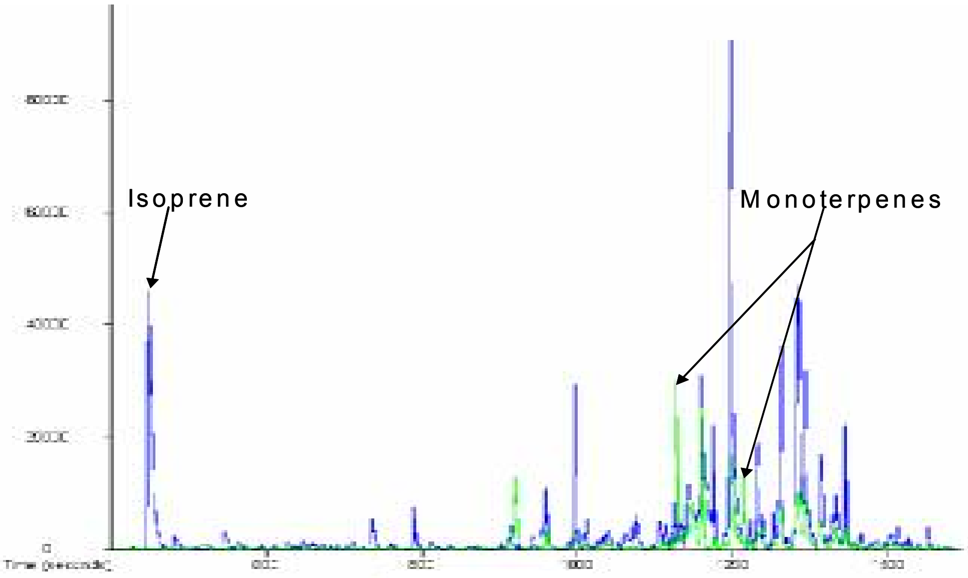

Figure 2. GC-MS analysis of biogenically influenced summertime rural air.

Typically monoterpene emissions have been seen to have a solely temperature related response in terms of emissions flux and so they too are strongly coupled to climate. One of the more uncertain factors relating to future monoterpene influence on air quality is not only in their temperature response but in how vegetation distribution will influence the types of monoterpenes emitted. Anthropogenic induced changes in vegetation type are a societal response to climate change, for example through the planting of crops for fossil fuel replacement. An example of a switch in both emission magnitude and in chemical speciation can be seen in the replacement of indigenous plant species in West Africa with alternative cash crops. Southern Sudanian vegetation-type zones characterised by woodland savannah comprising *Isoberlinia* species gave typically low ambient (200-400 pptV) abundances of alpha pinene as the major BVOC. However where non-native species such as Cashew (*Anacardium occidentale*) had been planted the monoterpene limonene became the dominant BVOC emission and was observed at concentrations as high as 5000 pptV [Saxton *et al.* 2007].

A final important uncertainty relating to the influence of biogenic emissions on air quality in the future is the impact of larger C_{15} and C_{20} sesquiterpene and diterpene species. Figure 3 shows monoterpene and sesquiterpenes seen in ambient air at the Beninese location used by Saxton *et al.* [2007].

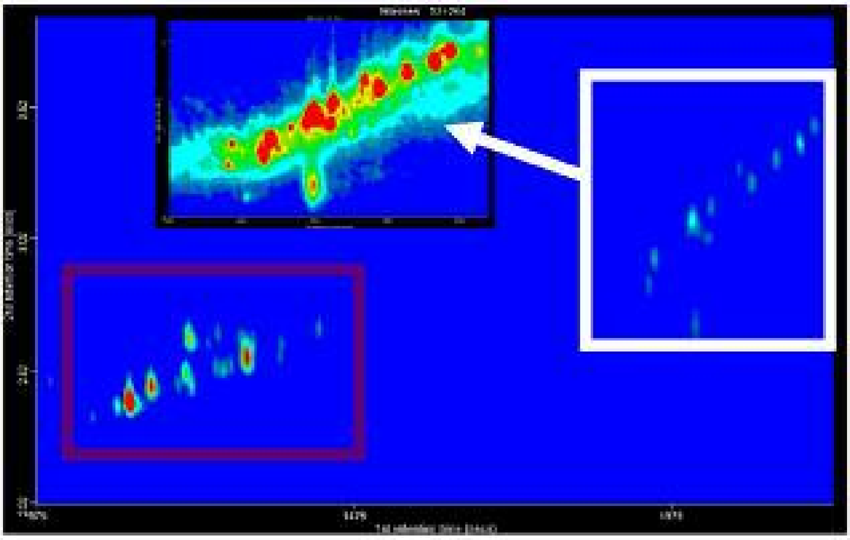

Figure 3. GCxGC-TOF analysis of adsorbent tube samples from Benin. Ozone and NO_2 scrubbed from sample line prior to sampling. Blue box, monoterpenes, White expanded box, sesquiterpenes.

The influence of such compounds is likely to lie mainly in the perturbation of fine particle numbers and distribution rather than ozone, however very few measurements exist due to compound involatility and high reactivity with ozone and other gaseous species. Indeed much evidence for their presence as active participants in photochemistry is *via* indirect methods such as total OH reactivity and total peroxy radical abundance. An analysis of compounds of this type in biogenic influenced regions does indeed show their presence, but species identification is extremely difficult. Additionally for most species there are no known chemical degradation pathways and mechanisms and rate constants can be estimated only from structure activity relationships. For this class of compound we can only currently make guesses at future climate response and subsequent impacts.

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Identification of Sources of Halocarbons on a Global Scale using the CARIBIC Experiment

A contribution to ACCENT CCAQ: Group 1

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The CARIBIC experiment uses a long-range commercial aircraft equipped with a container containing many real-time instruments and air sample collectors to determine the composition of the upper troposphere/lower stratosphere (UTLS) on a near global scale. The surface origin of the air samples collected in the UTLS during CARIBIC has been investigated using a 3-D particle dispersion model (FLEXPART). Figure 1, 2 and 3 show the combined surface footprints of the samples with the highest (top 10 %) concentrations of three individual halocarbons, methyl chloride (CH_3Cl), HFC-134a (CF_3CH_2F) and bromoform ($CHBr_3$).

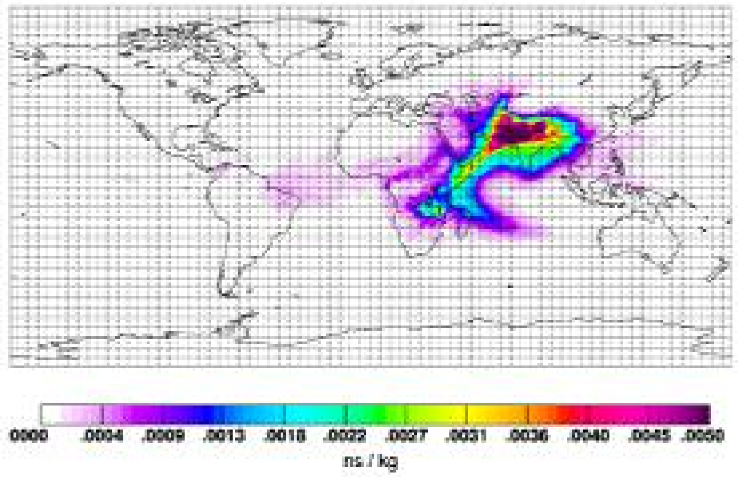

Figure 1. CH_3Cl

These footprint plots show the residence time of particles in the lowermost layer of the model grid (0-150 m) and reflect the geographical regions where surface emissions will have contributed to the mixing ratios measured in each sample. There is a striking difference in the geographical regions where the sources of the three compounds are located. The highest levels of methyl chloride seen in the CARIBIC samples have an origin in Asia and Africa, and are associated with biomass burning (including domestic cooking/heating) in these regions and possibly terrestrial emissions from certain plants that are known to occur, particularly in tropical and sub-tropical regions. HFC-134a, in contrast, is exclusively anthropogenic in origin, used in refrigeration and air conditioning applications, particularly in the developed world.

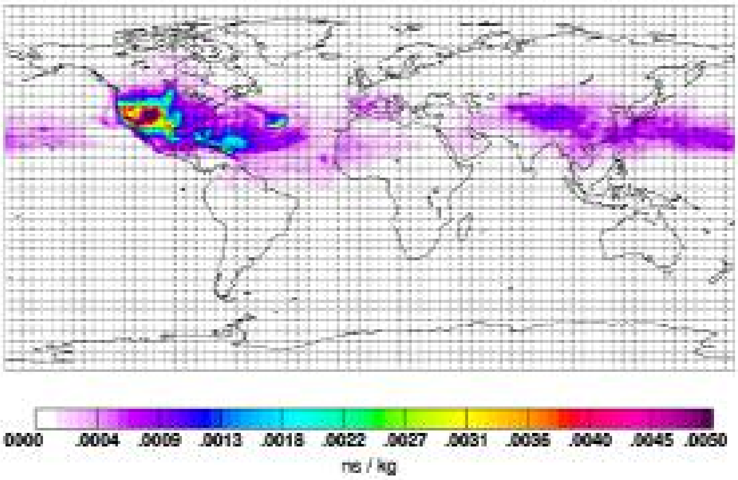

Figure 2. HFC-134a

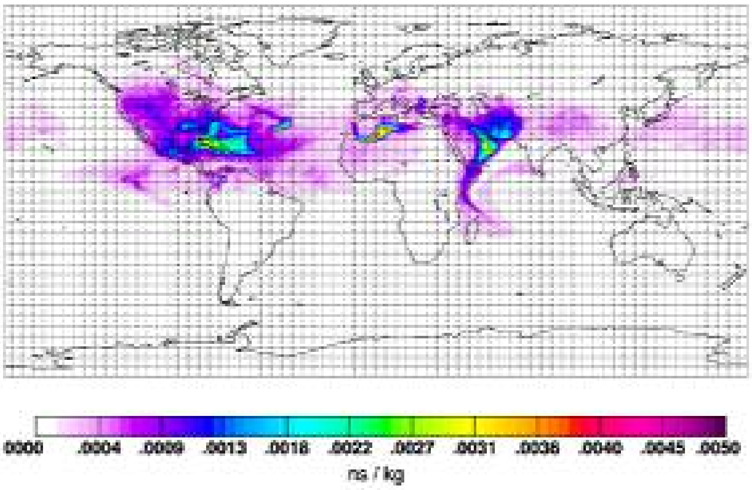

Figure 3. $CHBr_3$

As seen from the figure, the source region for the highest concentrations seen during CARIBIC was the USA, with little evidence of any major use in Asia. Bromoform is a natural compound produced in the oceans, particularly from macroalgae such as seaweeds. The highest concentrations seen in CARIBIC appear to emanate from the Gulf of Mexico (and other coastal locations). Bromoform is an important natural source of organic bromine in the lower troposphere but, despite having a relatively short atmospheric lifetime (26 days), may still contribute to stratospheric ozone loss. The FLEXPART analysis can be applied to any molecule or combinations of molecules. There is a real possibility therefore that halocarbon analysis can be used to identify individual continental sources for molecules other than halocarbons including of course greenhouse gases. This is an example of the power of detailed atmospheric chemical knowledge to act as a tracer of global emissions. The UEA involvement in the CARIBIC experiment was a component of the UTLS Ozone programme funded by NERC.

On the Usage of VOCs for Determination of Processes in the Background Atmosphere

A contribution to ACCENT CCAQ: Group 1

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Summary

Continuous measurements of volatile organic compounds (VOCs) at the high-Alpine site of Jungfraujoch (Switzerland, 3580 m a.s.l.) can been used for the determination of both atmospheric processes and changing anthropogenic emissions. The comparison of these background measurements with those from an urban site (Zurich) and those from a rural site (Rigi, Switzerland) show a shift to more stable VOCs at Jungfraujoch. Furthermore, oxidised VOCs, which are both originating from the decay of VOCs and emitted from biological sources become more important.

In the last years a decline in the VOCs representing the cleanest air masses has been observed at Jungfraujoch. This can be seen as an indication of European continuously getting lower. On the other hand no decline in background ozone has been observed, which could be due to the fact that emissions from Asia have increased substantially and contribute to the background concentration of ozone.

Introduction

VOCs have first been measured in Los Angeles during the notorious air pollution problems of this region in the 1950s [Eggertsen and Nelsen, 1958]. After different technical and political measures to curb emissions of VOCs and other air pollutants from exhaust gases (*e.g.* NO) have been put in place problems the air quality within cities of the developed world could be drastically improved. As an example the concentrations of benzene and toluene have been declined dramatically in the Los Angeles area within the last 50 years (see Figure 1). However, due to growing economies especially in south-eastern Asia emissions of these gases still occur on a global level due to less developed technical measures in these regions of the world [Streets *et al*. 2000, Rao *et al.* 1997].

Long-term measurements of VOCs at Jungfraujoch are performed continuously since the year 2000. They have been used for the distinction of interhemispheric transport [Li *et al.,* 2005; Balzani-Lööv *et al*., 2007] and for the analysis of mountain venting processes [Henne *et al.,* 2005]. Results of these measurements will be discussed in relation to stations within the polluted boundary layer. The data sets will be analysed for temporal changes and implications regarding the background atmosphere will be assessed. Furthermore, although the station at Jungfraujoch is often situated within the undisturbed "free troposphere", periodically polluted air masses from the industrialized regions of Europe (*e.g.* Po-valley) are transported to the site. A statistical approach using trajectories will be shown by which potential source regions can be detected and their influence on the background atmosphere can be assessed (Legreid *et al*., 2007).

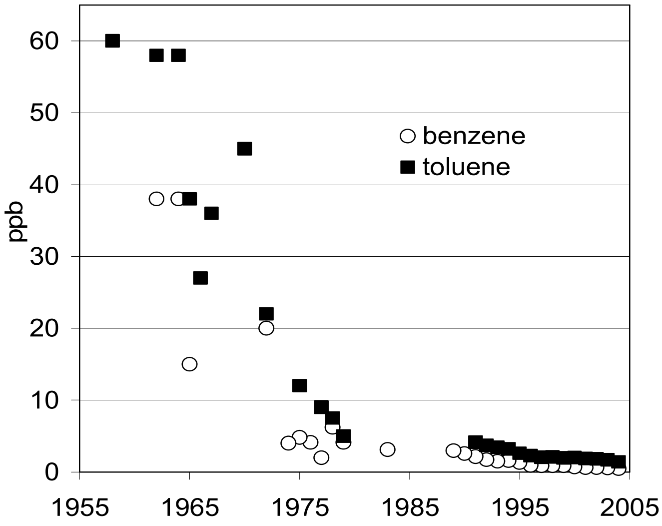


Figure 1. 50 years of benzene and toluene concentrations in California [Reimann and Lewis, 2007].

Scientific activities

Long-term measurements of VOCs at the high-Alpine station Jungfraujoch (3580 m a.s.l.) are analysed for both changes in their background behaviour and locations of European source regions. Due to the dense network of measurement stations in Switzerland these measurements can be assessed also for the influence of transport from the polluted atmosphere of Zurich to the rural site of Rigi (1080 m a.s.l.) and to the clean air site of Jungfraujoch.

Scientific results and highlights

As a measure of the effect of transport on atmospheric trace gases often hydrocarbons of different atmospheric lifetimes have been used [Roberts *et al.*, 1984]. Due to the availability of 4 measurement stations ranging from the city centre of Zurich, to a suburban site, to a rural site (Rigi) and finally the background site of Jungfraujoch this effect can be shown in an almost ideal way for the aromatic hydrocarbons (see Figure 2). Highest concentrations are measured in the city centre of Zurich. Values are already slightly lower at the suburban site of Dubendorf and decline to about a 15-40 % of their initial value when they reach the rural station of Rigi. Finally, at the high Alpine background site of Jungfraujoch (3580 m a.s.l.) concentrations decrease to 5-20 % of their urban concentration. Thereby, toluene and of C2-benzenes have declined faster than benzene because of their higher relative degradation in the atmosphere.

Data series of VOCs at Jungfraujoch have therefore the potential to be used as an indicator of the background atmosphere. As an example concentrations of benzene from 2000-2006 are shown in Figure 3a. Concentrations are higher in summer compared to winter due to smaller concentrations of the OH-radical and higher regional emissions from *e.g.* domestic heating and cold-starts of vehicles. When background concentrations are extracted from this dataset (Figure 3b) the seasonal cycle can still be seen.

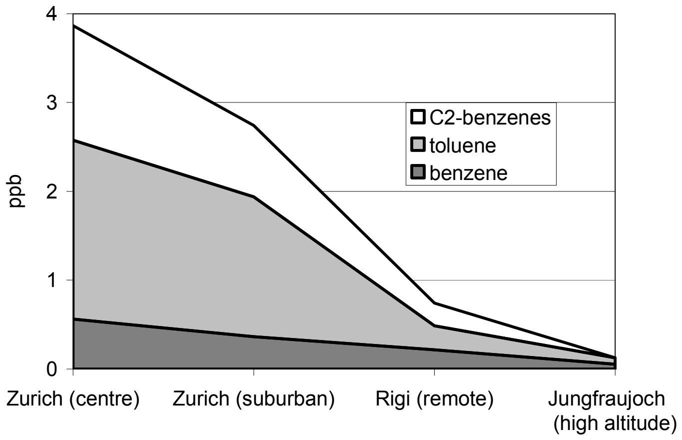
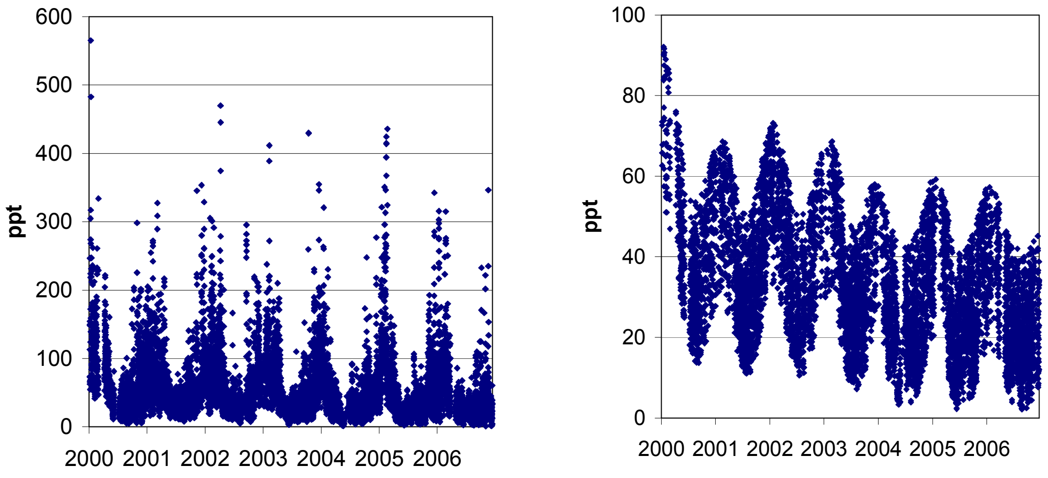


Figure 2. Annual mean concentrations of aromatic VOCs in 2003 at different sites in Switzerland, ranging from the polluted city centre of Zurich to the high Alpine site of Jungfraujoch.

Additionally a decline of the lowermost values can be seen. This feature has not been described in the literature until now. We argue that this could be an indication of regional European sources getting lower over the timeframe of almost the last decade. Intercontinental transport seems not to make up for the difference, although benzene has a lifetime in the range of weeks, which could be enough to actually transport at least a part of the exported pollution of South-East Asia to Europe. However, as Legreid *et al.* [2007] show that the OVOCs, which are dominantly produced during the decay of VOCs, are the prevailing compounds in the background atmosphere of Jungfraujoch. Therefore, we assume that regional sources of benzene and other long-lived VOCs are still dominating the background concentrations in Europe and that the major part of the extra-European VOCs has already been reacted. However, if emissions will continue to increase especially in south-eastern Asia, this could lead to a renewed growth of these substances in the European background atmosphere.


a)

b)

Figure 3. a) Data series of benzene at Jungfraujoch from 2000-2006. b) Data series of background concentrations at Jungfraujoch 2000-2006.

For the detection of regional European sources we apply a straightforward statistical trajectory model. Arriving trajectories are labelled with their respective concentration above the background and the averaged information from contributing grid cells can be used as an indicator for important European source regions. In Legreid *et al.* [2007] it could be shown that for example the region around Genoa in northern Italy and Germany are important sources for *n*–butane and benzene (Figure 4).

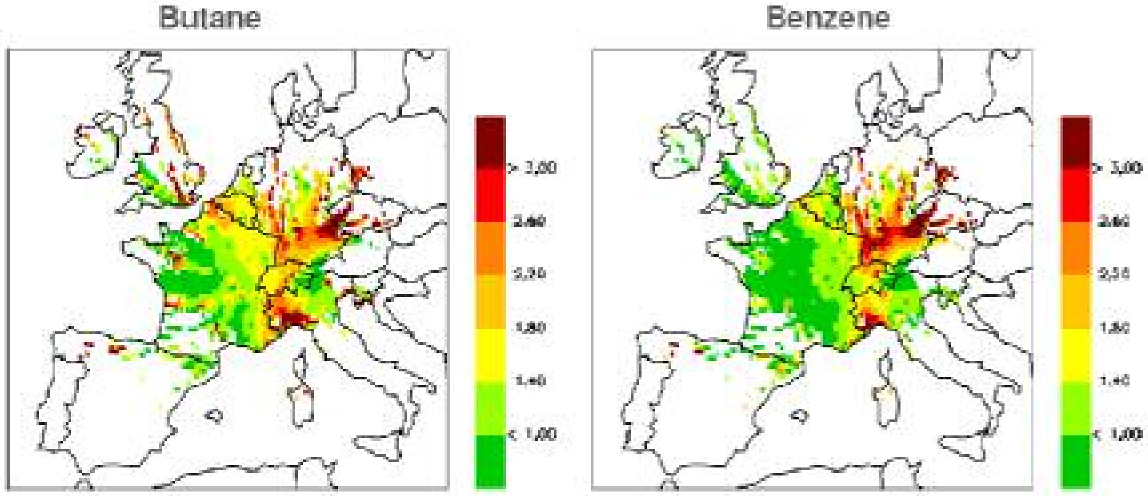


Figure 4. Map of potential source regions of n-butane and benzene from about four months of measurement data in 2005/06, as determined by statistical trajectory analysis. Colours give relative importance of regions for measured above baseline mixing ratios at Jungfraujoch. Red colours indicate regions which are, on average, associated with high mixing ratios above baseline measured at Jungfraujoch. Green colours are associated with, on average, small above baseline mixing ratios at Jungfraujoch.

Future outlook

The abundances of anthropogenic atmospheric VOCs generally decline from the polluted urban areas towards the clean background sites. The relative contribution of different VOCs to the concentrations in the European background seems to be relatively stable in the last decade. Concentrations of all major VOCs have been seen to decline at Jungfraujoch, indicating the success of technical and political measures to curb emissions of these substances. However, as emissions especially in south-eastern Asia are increasing a growing input from intercontinental transport could outweigh this development. Therefore, monitoring of the VOCs can act as an indicative tool for detection of global changes related to shifting economies. Furthermore, it could eventually also be used to protocol future curing measures in the regions of the world, where this is not in place at the moment.

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Impact of Changing Air Transport Patterns on Observed Trends of Surface Ozone in Europe

A contribution to the ACCENT CCAQ: Group1

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Summary

The impact of changes in air transport patterns on trends in surface ozone in Europe is discussed. A simple statistical approach is used to evaluate the component of the surface ozone concentration trend that is connected with a redistribution of air transport sectors. Data of the surface ozone concentration and daily transport sectors for 48 sites of the EMEP network are used. Estimates cover the period 1990-2004. It is shown that sectors redistribution can explain in average from 31 to 47 % of the observed trend of the surface ozone concentration. The influence of transport changes on ozone trends is more important for summer.

Introduction

Tropospheric/surface ozone is a major active photo-oxidant and a minor greenhouse gas. Several processes are contributing to the variations of its concentration, including photochemical production and destruction, horizontal and vertical transport, dry and wet deposition. Since the beginning of the 1990s peak ozone concentrations over Europe are decreasing [TOR-2 annual report, Jonson *et al.*, 2006 and references therein] while the background ozone concentration is increasing [Simmonds *et al.*, 2004; Brönnimann *et al.*, 2002; Ordóñez *et al.*, 2005]. The reasons for background ozone growth are still unclear. One of the possible explanations of the positive trend at the elevated European sites has been proposed by Ordóñez *et al.* [2007], who suggested that an increased contribution of stratospheric ozone was the main reason for the tropospheric ozone increase in the 90s. Modern CTMs used to evaluate ozone trends are able to explain only a part of winter concentration increase and decrease in high ozone episodes [Jonson *et al.*, 2006], but the changes in the background levels can not be explained yet.

Atmospheric transport substantially impacts the level of surface ozone concentrations. Auvray and Bey [2005] showed, that over Europe, the total background accounts for 30 ppbv at the surface. North American and Asian O_3 contribute substantially to the annual O_3 budget over Europe, accounting for 10.9 % and 7.7 %, respectively, while the European contribution only accounts for 9.4 %. Sudo and Akimoto [2007] reported that O_3 transport from the polluted source regions like North America, Europe, and Asia generally accounts for more than 40 % of ozone abundances even in remote locations. There are many papers showing the influence of the long-range transport on the ozone levels in the troposphere [Stohl *et al.*, 2002; Stohl, 2006; Wild *et al.*, 2004].

Atmospheric transport influences tropospheric ozone variability from diurnal to decadal scale, and it can change of course as a consequence of the global circulation changes. Cape *et al.* [2000] reported the inter-annual variability of the air transport patters observed at Mace Head, Ireland. Moreover he has shown, that a clear difference in ozone concentration was observed for different clusters. Creilson *et al.* [2003] showed a strong correlation between the phase of the NAO and transport of tropospheric ozone across the North Atlantic to Europe. In our earlier work we showed that strong correlation between transport indices and surface ozone anomalies observed over Europe [Tarasova *et al.*, 2004]. A clear connection between air transport patters and surface ozone trends at elevated sites was also reported [Tarasova *et al.*, 2003; 2007].

In this paper an attempt is made to summarize the diversity of the surface ozone concentration responses on the changing air transport patterns at different locations in Europe and to estimate the part of the surface ozone concentration trend connected with changing horizontal advection.

Mathematical approach

We use for our analysis surface ozone concentration measurements from the EMEP network (www.emep.int). Only the long data sets covering the period from 1990 to 2004 are considered, and daily averaged concentrations are used. Air transport patterns are represented by daily sectors variations. The daily sector values are based on 96 h backwards 2-D trajectories. The area around the arrival point is divided into 8 equal sectors. Sector 1 (North) ranges from −22.5 degrees to 22.5 degrees. The next sectors are spread clockwise. The area around the arrival point extends from a radius of 150 km to a radius of 1500 km. The criteria for allocation of trajectories to one sector is that at least 50 % of its given positions are found within that sector. Otherwise, trajectories are allocated to sector 9 (non-attributable. The daily sectors are available simultaneously with the log-term ozone records only for 48 EMEP sites.

To evaluate the impact of the air transport on the surface ozone concentration a simple statistical approach is used. For each site the following datasets are retrieved: surface ozone concentration $O_3(d,m,y)$ and daily sector $S(d,m,y)$, where d, m, y are day, month and year of measurements. Mean seasonal cycle of ozone concentration is calculated for each site like following:

$$\overline{O}_3(m) = \frac{1}{N_{y,d}} \sum_{y,d} O_3(d,m,y),$$

where $N_{y,d}$ is a total number of the measurement points for each particular month for all years and days of measurements.

In the same way a mean seasonal cycle is calculated for each sector frequency:

$$\overline{N}(m,S) = \frac{1}{N_y} \sum_{y} N(m,y,S),$$

where $\overline{N}(m,S)$ is a monthly average frequency of each sector S for the whole measurement period and $N(m,y,S)$ is a monthly frequency of each particular sector for each year of the measurements.

Mean deviations of the seasonal cycle for the each particular sector from the average seasonal cycle are calculated:

$$\Delta\overline{O}_3(m,s) = \frac{1}{N_{y,d,s}} \sum_{y,d} (O_3(d,m,y)/s) - \overline{O}_3(m).$$

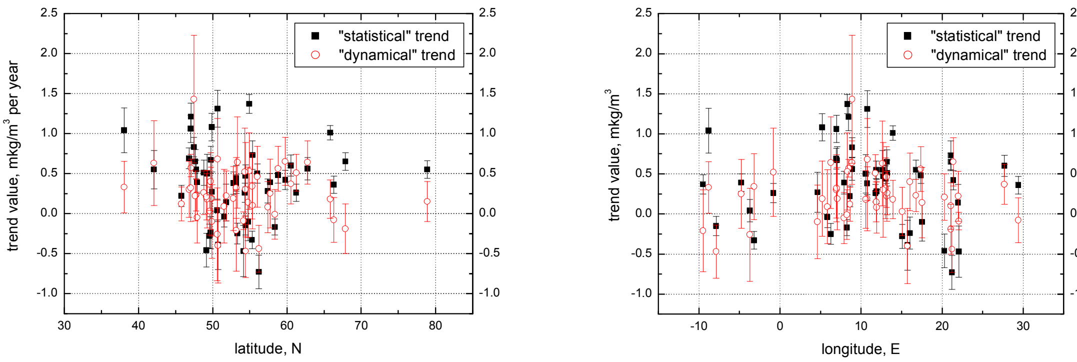
The resulting deviations do not depend on the year, but depend on the month and reflect the seasonality of the average spatial gradients. Multiplying the obtained “mean deviation” by the relative frequency of each sector in a particular year we estimate the variations of the surface ozone concentration caused by the predominance of different sectors in different years:

$$\Delta O_{3,i}(m,y,s) = \Delta\overline{O}_3(m,s) \times N'(m,y,s) / \overline{N}(m,s)\,.$$

By summarizing the last value for all sectors we obtain a quantity, referred to in the text as “dynamical anomalies”. The corresponding slope of the time regression line is called “dynamical trend”. This trend reflects only a part of the total trend connected with a changing frequency of the sectors. At the same time it should be understood that ozone concentration also changes in the “source areas”, or “areas of advection”. Hence, the dynamical trend does not bear the total information on trends. As a “statistical anomalies” we understand the deviations of the monthly mean ozone concentration in particular year from the averaged one for the period 1990-2004. The corresponding slope of the time regression is referred to as “statistical trend”. The impact of the non-attributed transport can be also substantial.

Results and highlights

The trends of the surface ozone concentration depend on many parameters from local to global. Even for adjacent locations they can be substantially different. The range of the average statistical trends for the considered sites is from −0.73 μg/m^3 to +1.37 μg/m^3. Note, that statistical trend and daily mean concentration trend are not the same quantities. In half of the cases trend uncertainty (slope standard deviation) does not exceed 30 % of the absolute trend value, and hence trends can be considered as statistically significant. Only in 4 cases standard deviation of the trend exceeds trend value. At 12 locations the trend is negative and it is positive at the rest of sites. The range of the average “dynamical” trends for the considered sites is from −0.47 μg/m^3 to +1.4 μg/m^3. It is negative at 11 locations and positive at the rest of sites. There is only one location (Rigi) where uncertainty of the dynamical trend detection is less than 20 %. At 16 locations the trend uncertainty is less than the trend value and at the rest trends are statistically non-significant.



(a) (b)

Figure 1. Dependence of the “statistical” and “dynamical” trends of the surface ozone concentration on the sites’ latitude (a) and longitude (b) is presented for the 48 locations considered. The error bars show one standard deviation of the trend detection.

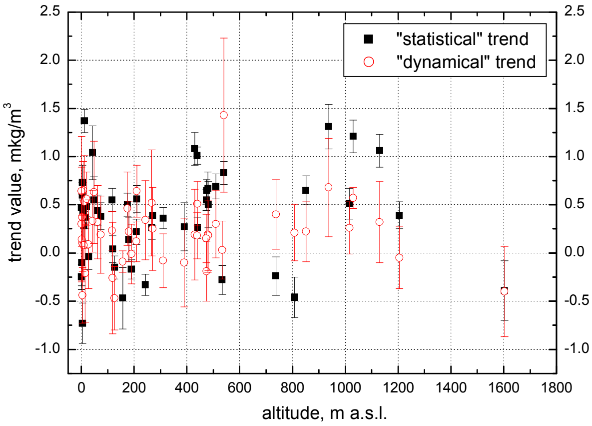


Figure 2. The same as in Figure 1 but as a function of the site altitude.

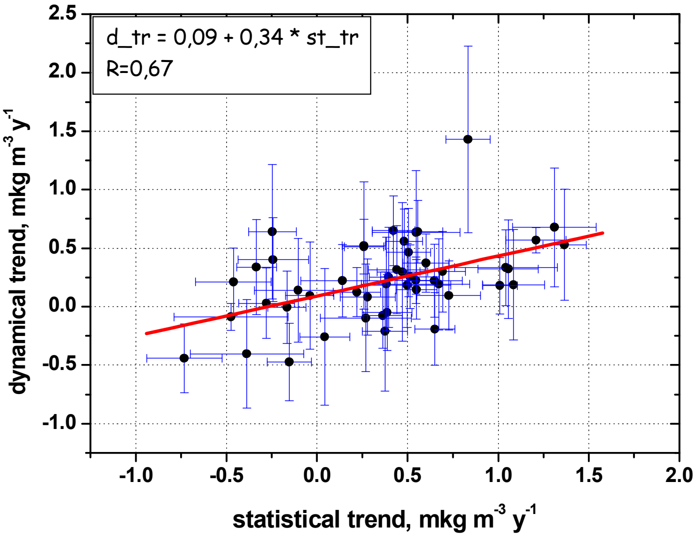


Figure 3. Scatter plot of the "dynamical" trend against the "statistical trend" is presented. Linear fit gives an average dependence of the "dynamical" trend on the statistical one. The equation is presented on the graph.

There is no systematic dependence of the trends either on the geographical location (latitude or longitude) (Figure 1) nor on the site altitude (Figure 2). Actually, mountain locations are poorly represented in analysis.

In Figure 3 it can be seen, that dynamical trends are in general lower than statistical trends. The majority of sites lay in the areas of "positive-positive" trends in the graph, but for some sites statistical and dynamical trend can have different signs. Usually dynamical trends are shifted to more negative values. The correlation between statistical and dynamical trends is positive and relatively high (0.67). Retrieved regression equation is presented on the graph. In average the dynamical trends constitute up to 34 ± 5 % of the total trend. The part of the explained trend can differ substantially from one location to another.

In general winter trends are more positive than the total (Figure 4), but for some particular locations this shift is less pronounced. The dynamical trend changes are less spatially uniform. This causes weakening of the relation between statistical and dynamical trends. It is very likely, that other factors than transport (*e.g.* a decrease of ozone by titration with NO) influence winter trends. Correlation between dynamical and statistical trends is only 0.33. The slope of the regression line (Figure 4) shows that the part of total trend which can be connected with the transport patterns changes constitute 38 ± 15 %.

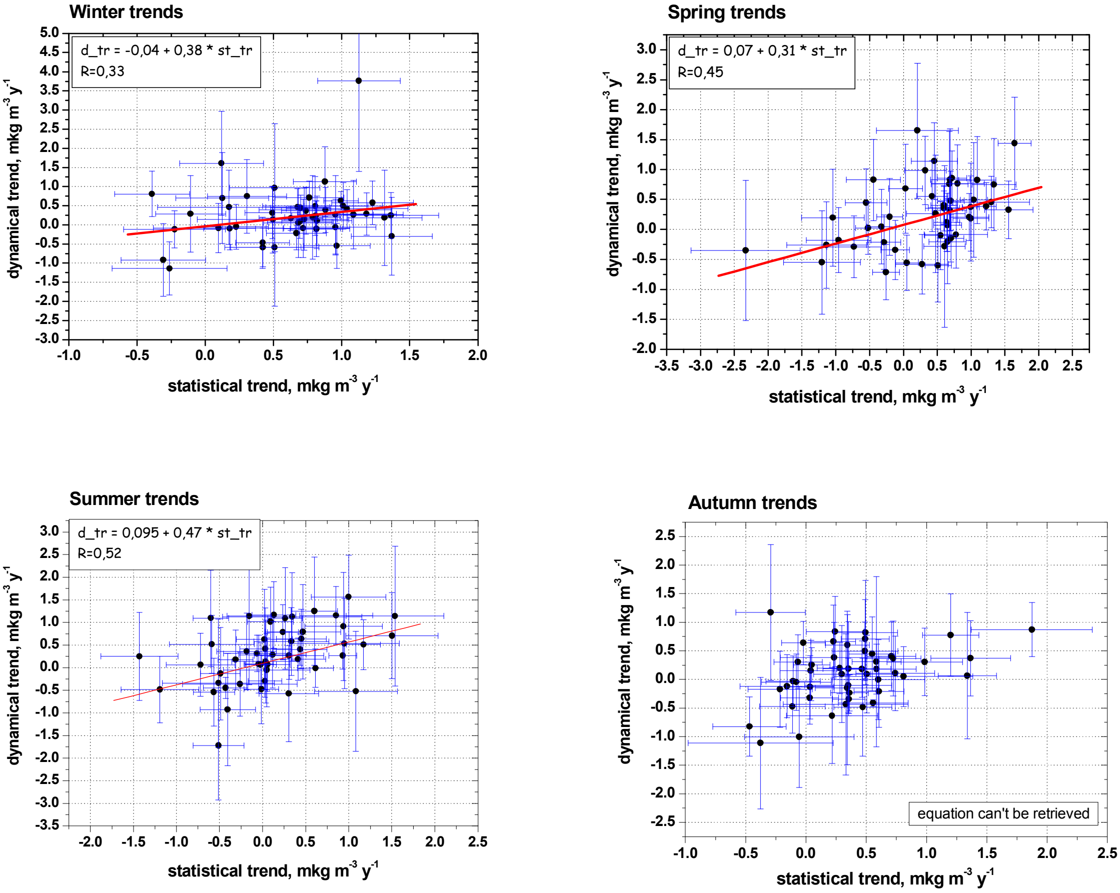


Figure 4. The same as in Figure 3 but for different seasons.

For spring months both statistical and dynamical trends become more negative than average. Correlation between them is higher than for winter months but still lower than average (0.45 against 0.33 and 0.67). The slope of the regression line of dynamical trends against statistical trends shows, that the part of the statistical trend, which can be explained by transport patters changes in spring reaches only 31 ± 9 %, which is even less than in winter. This means that even a lower part of spring trends in comparison with winter can be connected with horizontal advection changes and that other factors (like STE or local production/destruction terms) are more important for spring trends.

Summer dynamical trends become more scattered than the total dynamical trends and more shifter to the positive values. This means that due to transport changes the positive ozone trends in summer should be more positive that in the other seasons. The connection between dynamical trends and statistical trend is the strongest during summer in comparison with the other seasons (R = 0.52). In summer the part of the statistical trend which can be connected with air transport pattern changes rises up to 47 ± 11 %. This indicates higher significance of the horizontal transport for the surface ozone concentration variability in summer as far as spatial gradients are more pronounces during this season.

In autumn the trends are comparable to the overall trend (Figure 4) but the relation between statistical and dynamical trends is very weak. The regression line based on the scatter plot is statistically not significant due to big uncertainty of both types of trends in autumn.

Future outlook

The preliminary results we presented show the importance of the horizontal advection for the surface ozone trends formation. The highest sensitivity to the air transport changes is observed for summer due to more pronounced spatial gradients of the surface ozone concentration in comparison with the other seasons. For summer nearly half of the ozone trends can be associated with a re-distribution of the advection sectors. The applied approach has a number of limitations: it takes into consideration daily sectors covering in space the area from 150 to 1500 km from the site location, and hence more representative for local or regional transport; 2) the sign of the spatial gradients is supposed to be similar for different years as far as an average deviation of the seasonal cycles in each transport sector is used for estimates. To make the estimates more efficient we plan to use real trajectories in the future. That can give additional information as it will help to discrimination between night and day trends.

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Global Signal as Observed from Space: Is the Anthropogenic Contribution Important?

A contribution to ACCENT CCAQ: Group 1.

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Abstract

This study focuses on the observation of glyoxal column densities above photochemically active "hot spots" areas where enhanced intensive biogenic, anthropogenic and biomass burning emissions occur. Special attention is given to the evaluation of the importance of the oxidation of anthropogenic precursors to the observed glyoxal levels relative to the biogenic ones, in places affected dominantly by humans (*e.g.* China and Europe) since our knowledge for the anthropogenic precursors forming glyoxal is currently limited. For this reason the 2003-2007 irradiance observations by SCHIAMACHY are analyzed to extract information on the CHOCHO vertical column levels above specific geo-locations and on its seasonal and annual variations. The existence of potential trends is also investigated.

The satellite data are reasonably reproduced by the 3-dimensional global chemistry transport model TM4. The model calculates that about 70 % of the observed glyoxal column above the industrialized areas is due to anthropogenic precursors highlighting the importance of human induced emissions for glyoxal levels. The differences between the satellite observations and the model results point to existing gaps in our understanding of the complex chemical system that is driving the levels of glyoxal in the troposphere.

Introduction

The importance of Volatile Organic Compounds (VOC) is mainly issued from their influence on climate by: a) ozone production and b) secondary organic aerosols (SOA) formation. VOCs are emitted by anthropogenic, biogenic and biomass burning sources but also they are produced indirectly during the transformation of primary VOCs. Note that about 90 % of the VOC emissions are from the biosphere and therefore are climate driven. Given their short lifetime, several VOCs can be found almost exclusively near the sources areas. The large number of VOCs present in the atmosphere imposes the study of secondary species distributions that are produced during the oxidation of primary VOC. Some of these secondary compounds are considered as key intermediates of the total oxidation processes and the study of their mixing ratios or/and column densities will add substantial information to our understanding of the chemical processes in the atmosphere. Among these species is the glyoxal (CHOCHO), which has only recently being observed from space [Wittrock *et al.,* 2006]. Given the short lifetime of CHOCHO (1.5-6 hours) [Volkamer *et al.*, 2005; Fu *et al.,* 2007; Myriokefalitakis *et al.*, 2007] this molecule can be used as a good indicator for areas with enhanced photochemical activities.

Glyoxal is a small dicarbonyl compound with characteristic absorption peaks mainly at the VIS region (425-457nm). The measurements are conduced by the SCIAMACHY instrument which is on board of the ENVISAT satellite. It is designed to measure sunlight, transmitted, reflected and scattered by the Earth's atmosphere or surface in the ultraviolet, visible and near infrared [Burrows *et al.,* 1995]. The sun-synchronous, near polar orbit of the satellite has a local equator crossing time of 10:00am and global coverage is achieved within 6 days. The respective analysis of the data is performed by applying the Differential Absorption Optical Spectroscopy [Platt, 1994] and then converting the obtained slant columns (SC) to vertical columns (VC) via an air mass factor.

The measurements have been compared comparison with the results of the 3-D global atmospheric chemistry transport model TM4, [Myriokefalitakis *et al.,* 2007] and the model has been further applied to analyze CHOCHO budget. TM4 has 31 vertical hybrid layers from the surface to 10 hPa and can run in two different horizontal resolutions, the low resolution of $6^o \times 4^o$ in longitude and latitude and the high resolution of $3^o \times 2^o$. The model's input meteorology comes from the ECMWF operational data for 2005 and is updated every 3 to 6 hours.

Scientific results and highlights

The mean glyoxal vertical column densities retrieved from the SCIAMACHY observations during the period 2003-2007 are depicted in Figure 1.

As observed, glyoxal values range from below the detection limit (2×10^{14} molecules·cm^{-2}) to 1×10^{15} molecules·cm^{-2}. In some cases, the monthly mean values exceeded the 10^{15} molecules·cm^{-2} level (not presented here).

As shown in Figure 1, glyoxal presents enhanced columns both above regions with biomass burning activities and regions with intense biogenic emissions (*e.g.* east coast of USA). A clear glyoxal signal can be also identified when focusing above megacities. The observed annual mean vertical column of glyoxal (VC_{CHOCHO}) above the 30 most populated areas of the globe was 3.5 (± 2.0) × 10^{14} molecules·cm^{-2}. This value is about 30 % lower than CHOCHO columns observed above biogenic emission regions. Remarkably, the vertical columns of formaldehyde extracted for the anthropogenically and biogenically influenced selected areas were about the same. Therefore the ratio of CHOCHO/HCHO is larger above the biogenic regions (0.050 ± 0.025) in comparison to that over the anthropogenic regions (0.037 ± 0.014).

During summer the CHOCHO produced from VOC species oxidation dominates glyoxal removal by photodissociation and oxidation mainly by the OH radicals, leading to a net increase in glyoxal column compared to winter. On the opposite, during winter the balance between production and removal results to lower vertical CHOCHO columns, possibly due to both the lower photochemical production of glyoxal that is initiated by the low wintertime OH levels and increased removal by wet deposition.

To further investigate glyoxal formation from anthropogenic precursors and its seasonal variability, the global 3-dimensional chemistry transport model of the troposphere TM4 has been used. The chemical production of glyoxal is calculated to equal about 55 Tg y^{-1} with 75 % produced from biogenic hydrocarbons oxidation, 14 % from acetylene, 3 % from ethene and propene and 8 % from aromatic chemistry [Myriokefalitakis *et al.*, 2007]. Above the industrialized areas mainly in the northern hemisphere, up to 70 % of the CHOCHO column is linked to anthropogenic precursors. Finally, the characteristic

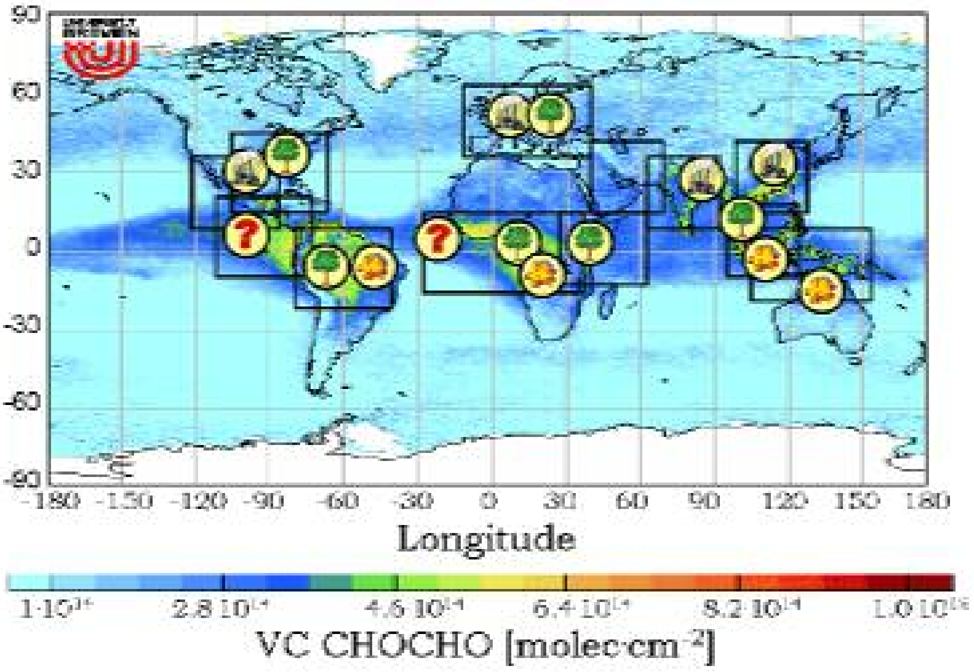

Figure 1. Global multi-annual composite of CHOCHO as observed by SCIAMACHY for the period 2003-2005. High values of CHOCHO are observed above industrial areas (factories), biogenic sources (trees), biomass burning (fire) and oceans (question mark).

seasonal variation retrieved from SCIAMACHY data above both biogenic and anthropogenic sources is also reproduced from the model simulations. In general, the satellite and modeled results are in a good agreement, nevertheless differences above areas with enhanced VC_{CHOCHO} values, for example, above oceans, provide space for further improvements.

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Long-term Observations of Nitrate Radicals in the Marine Boundary Layer of a Remote Area.

A contribution to the ACCENT CCAQ: Group 1

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Summary

Nitrate (NO_3) radicals are among the three major oxidants in the troposphere. Extended observations of nitrate (NO_3) radicals were performed in the atmosphere over the north coast of Crete Island in Greece (Finokalia station) for more than two years (2001-2003). Average NO_3 values were found to follow a distinct seasonality. The highest mixing ratios were observed in summer (5.6 ± 1.2 pptv) and the lowest in winter (1.2 ± 1.2 pptv). Concurrent measurements of ancillary chemical species and meteorological parameters conducted at Finokalia, revealed that NO_3 correlates positively with temperature and negatively with relatively humidity (both climate driven parameters) and to a lesser extend with ozone (a pollutant and a greenhouse gas). The analysis pointed out that for this area the major sink of the nitrate radicals is the heterogeneous reaction of dinitrogen pentoxide (N_2O_5) on aqueous particles. However, the gas phase reactions proved to have an elevated importance during spring and early summer. Chemical interactions of naturally emitted dimethylsulfide and isoprene with NO_3 radicals of human origin are evaluated to be a significant source of nutrients in the area.

Introduction

NO_3 radicals are among the three most important oxidants of the troposphere together with OH radicals and ozone molecules. They regulate the self cleaning efficiency of the atmosphere and consequently the quality of the air and the climate itself. Nitrate radicals undergo gas phase reactions with Volatile Organic Compounds (VOCs) [Atkinson, 2000]. Depending on the reaction rates of VOCs with the atmospheric oxidants, there are several compounds which are more reactive towards NO_3 than hydroxyl (OH) radicals. For example, dimethylsulfide (DMS) [Vrekoussis *et al.*, 2004], isoprene [Liakakou *et al.*, 2007], monoterpenes, alkenes, aromatics are among those species. NO_3 radical reactions also contribute to the conversion of NOx to reactive nitrogen [Allan *et al.*, 2000] forming nitric acid (HNO_3) and particulate nitrate (NO_3^-) [Brown *et al,* 2004; Vrekoussis *et al.*, 2006] and subsequently removal by wet and dry deposition.

Due to the high spatial and temporal variability of NO_3 radicals, only a limited number of observations of these species are available in the literature [Carslaw *et al.*, 1997, Allan *et al.*, 2000, Brown *et al.*, 2003; Saiz-Lopez *et al.*, 2006] and even less provide long-observations [Heinz *et al.*, 1996; Geyer *et al.*, 2001; Vrekoussis *et al.*, 2007].

Scientific activities

The objective of this work was to monitor nitrate radical levels on a long time scale, to identify the factors controlling their mixing ratios and their production rates, as well as to provide information on their sinks and the respective consequences to the biogeochemical cycling of nitrogen.

The NO_3 radicals were retrieved from spectra obtained using a long-path differential absorption spectroscopy instrument - DOAS (10.4 km - Xe 500W lamp). NO_3 is detected in the VIS region. Supportive information for understanding of the NO_3 chemistry has been obtained from observations of relevant chemical compounds and meteorological parameters. Special focus is put on the study of the two major precursors of NO_3, nitrogen dioxide (measured by DOAS) and ozone (measured by a UV absorption instrument - Dasibi).

Scientific results and highlights

Monthly mean NO_3 radicals observations vary from below the pptv level to about 10 pptv with maximum values exceeding 120 pptv (Figure 1). NO_3 radicals presented a clear seasonal variation with higher values in summer and lower in winter. The NO_3 radicals' annual average for the period June 2001 to September 2003 was 4.2 ± 2.3 pptv and their mean lifetime has been determined equal to 5 minutes. Single and multiple regression analyses of the NO_3 data in conjunction with a series of individual variable-parameters, namely ozone, nitrogen dioxide, radon, temperature, relative humidity and wind speed, revealed that NO_3 levels are mainly controlled by the temperature (positive correlation) and the relative humidity (negative correlation) and to a lesser extend ozone (positive correlation). These relationships indicate the existence of potential feedback mechanisms between climate, which is affecting temperature and relative humidity, and NO_3 driven chemistry, which is affecting the biogeochemical cycle of nitrogen and indirectly the levels of radiatively active atmospheric trace constituents like ozone and aerosols.

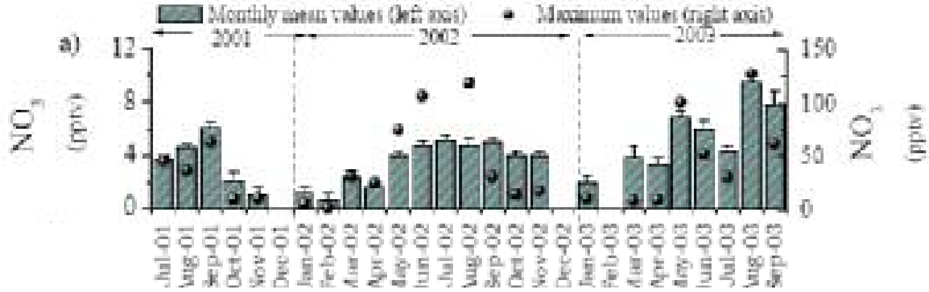

Figure 1. Monthly mean mixing ratios (left axis – bars) of nitrate radicals and their standard deviation. Black circles depict the maxima of NO_3 (right axis) [From Vrekoussis *et al.*, 2007].

Taking into account the respective reactions of NO_3 radical production and degradation, Vrekoussis *et al.* [2007] found that the major loss pathway of NO_3 radicals in this remote coastal region is the indirect loss via conversion to N_2O_5 followed by heterogeneous removal processes. This is supported by Figure 2a which presents scatter plots of the logarithmic correlation between the NO_3 lifetime and the NO_2 concentrations for different relative humidity values. Note that when the direct sinks are negligible, the NO_3 lifetime is proportional to the inverse of the NO_2 mixing ratio [Heinz *et al.*, 1997; Vrekoussis *et al.*, 2007]. The resulted slope is close to the “ideal” -1 under high relative humidity values, pointing to the existence of indirect sinks of NO_3 related to atmospheric water vapour.

However, direct losses from homogeneous gas phase reactions are not negligible and play a significant role in the night-time chemistry during spring and summer.

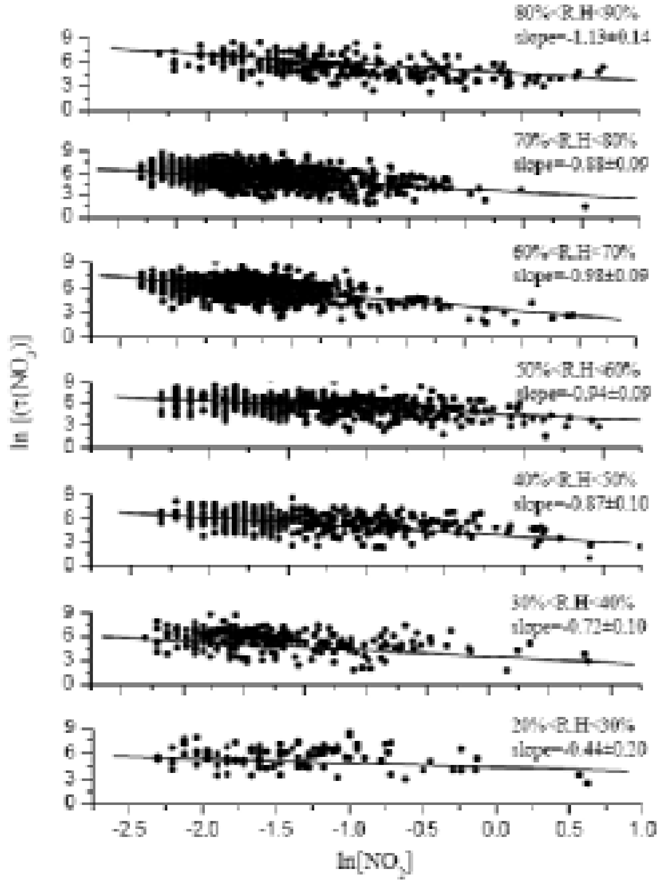

Figure 2. Correlation of the logarithm of the lifetime of NO_3 radicals and the logarithm of NO_2 at different humidity ranges (20 to 90 %) [From Vrekoussis *et al.*, 2007].

Finally, it was found that NO_3 radicals contribute about 50-65 % in the total production rates of nitric acid (HNO_3) and nitrates (NO_3^-) [Vrekoussis *et al.,* 2006], depending on the season. In addition, DMS reaction with NO_3 radicals contributes by 25-30 % to the diurnal mean HNO_3 formation in the area. The above demonstrate the importance of the nighttime chemistry and significant interactions between natural and anthropogenic emissions in the area. Both DMS natural emissions and NO_3 radical chemical sources and sinks terms are strongly affected by climate. In turn, since they affect aerosol and O_3 levels in the troposphere they feedback on climate. However, the extent of this feedback mechanism has to be determined.

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Transport and Transformation of Pollutants (T&TP)
Access to Emission Data, Access to Laboratory Data,
Aerosols, Remote Sensing from Space (AT2),
BIAFLUX, Modelling

AT2

BIAFLUX

11 Contributions from Group 2 Participants

Investigating changes in surface-atmosphere interactions with changing temperature and land use

Scaling Issues, with Particular Reference to Biogenic VOC Emissions

A contribution to ACCENT CCAQ: Group 2

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Summary

This contribution highlights recent issues concerning biogenic VOC emissions and the implications for scaling data and processes used in modelling both regional and global effects of climate change.

Introduction

The prediction of future effects of climate change on land surface/atmosphere interactions relies on accurate models of the driving forces and responses, so that present knowledge of processes and mechanisms can be used appropriately to forecast likely outcomes, based on a range of possible climate change scenarios. However, the models that are used have been developed for application at different temporal and spatial scales, and these are not always recognised when considering model outputs. At the global scale, climate change is usually modelled over periods of 20 – 100 years, and assumptions have to be made about what is likely to change (and can be modelled) and what may stay constant (or may be regarded as having little net effect over the time period). However, changes to some major drivers can sometimes be ignored because they are too difficult to measure or predict – of which changing land use is one of the most important.

Future patterns of land use

When considering scenarios for the emissions of biogenic VOCs the impact of land use, or quantity and quality of vegetation, is recognised as important in determining the types and amounts of VOCs emitted. The effects of temperature on BVOC emissions can be estimated based on the ‘Guenther algorithm’ [Guenther *et al.*, 1995, Simpson *et al.*, 1999], and a potential increase in emitting surface (above-ground biomass, or leaf area index LAI) based on the response of vegetation to increased carbon dioxide concentrations. Both effects would tend to enhance the magnitude of BVOC emissions, but are generally based on patterns of vegetation and land use that are typical of the current day. Although the effects of CO_2 ‘fertilization’ have been incorporated into estimates of future vegetation growth, the role of airborne nitrogen (N) deposition and increased mineralization of soil N [Bytnerowicz *et al.*, 2007] have not in general been included in such models [Cowling and Field, 2003]. Whether vegetation can utilise (man-made) additions of N to an ecosystem may well depend on the availability of other essential plant nutrients – the forest ‘decline’ in Germany in the mid 1980s was exacerbated by induced deficiencies in magnesium in forest soils [Schulze, 1989]. In general, our knowledge of future patterns of N emissions and deposition, and the role of soil composition in determining the overall effect on vegetation growth, is not well understood, nor yet incorporated fully into models.

However, we know that land use changes also occur on decadal timescales or less, driven by economic and social factors that have little directly to do with climate change. Not only are these likely to change the amounts of BVOC emitted, but also the types of

BVOC, with profound implications for subsequent atmospheric chemical reactions leading to formation of particles or ozone. Examples are the conversion of rain forest (isoprene/monoterpene emissions) to soya (oxygenated VOCs) or oil palms, or of arable crops to biofuels (*e.g.* poplar, a major isoprene emitter). Even without major changes, farmers are likely to use new varieties of crops that are more suited to their particular climate and soil regimes as these gradually change, and it is unlikely that the new varieties will have the same BVOC emission characteristics as the old ones. More generally, practices such as slash and burn agriculture will influence the extent of biomass burning and the associated VOC emissions.

Such changes affect large areas of land and are rapid on the time scale of most GCM/chemistry models aimed at predicting the state of the atmosphere in the latter half of this century. Details of the precise algorithms used, or the emission factors to be used for tropical vegetation, may be irrelevant compared to such changes. Moreover, climate change itself may lead to land use and vegetation changes that are not caused by economic or social factors, such as progressive desertification in some regions, increased vegetation growth in others, or increased risk of major pest-related damage. There is a clear need for better maps of current land-use (cover, species composition, growing season), and estimates of the uncertainties involved in extrapolating land use and vegetation changes globally into the future.

Timescales for change

Some information on the likely 'fertilizer' effects of CO_2 is already available from controlled experiments, especially now that large-scale experiments have been running over several years with mixtures of species [Karnosky *et al.*, 2007]. This led to recognition that processes of adaptation and acclimation occur in the field, and take time, and that predictions based on experimental manipulation under laboratory conditions over short time periods may not adequately represent the long-term (decadal) responses that are likely to occur as a result of increased CO_2 concentrations. Some of the other responses to climate change used in global models may be similarly inappropriate for predicting responses on decadal time scales. For example, the 'Guenther algorithm' for BVOC release was largely generated using temperature changes over a few hours on 'non-adapted' vegetation. This may be appropriate for looking at the release of VOCs from storage pools [Filella *et al.*, 2007], where the process involved is one of equilibration between dissolved and airborne material, but provides little information on the role of temperature changes in the induction of gene expression (which may take hours to days), or both intra- and inter-specific selection of better adapted genotypes (which may take years to centuries, depending on the plant type).

There has been recent debate as to whether increased CO_2 concentrations will inhibit isoprene emission from plants [Arneth *et al.*, 2007]. The evidence for this is clear from short-term experiments, but the long-term implications are not well understood [Calfapietra *et al.*, 2007], because it is not known whether adaptation and acclimation will occur. Attempts to model the process at a biochemical level may provide better understanding of the underlying drivers [Monson *et al.*, 2007], but will not necessarily predict the selection pressures that could lead to adaptation over decades. Similarly, there is evidence appearing that rates of BVOC emission from some species may depend upon the nutritional status of the vegetation [Ormeno *et al.*, 2007]; if enhanced vegetation growth, because of higher CO_2 concentrations or deposition of anthropogenic N, leads to nutrient depletion then there may be changes to the pattern of BVOC emission.

One of the climatic factors known to influence BVOC emissions is the soil water status. Reductions in water availability over hours or days can reduce BVOC emissions by restricting stomatal opening, but prolonged drought may lead to severe plant stress, and greatly enhanced BVOC emissions as an acute response. Separating these processes in modelling long-term changes is going to be difficult.

Spatial scales in models

One of the problems of accommodating dynamic processes in models that occur on different time-scales is the interaction between the dynamical changes and the spatial dimensions of the model. It has already been documented that the assumption of 'instant mixing' of the atmosphere within a numerical model cell leads to apparently faster chemical reactions, i.e. as grid cells are smaller and spatial resolution increases, the rate of production of ozone appears to decrease [Stevenson, *et al.*, 2006]. This can cause real problems of interpretation – a recent set of field and aircraft measurements of BVOC fluxes from tropical rainforest (which incidentally agreed reasonably well with predictions of 'bottom up' emission models) could only be reconciled with the measured air concentrations of the BVOC species by assuming that the actual hydroxyl radical concentrations (OH.) were an order of magnitude greater than used in the atmospheric chemistry models used to interpret the data [Kuhn, *et al.*, 2007]. This may have been a problem associated with spatial heterogeneity, or may highlight our deficiencies in understanding rapid reactions of BVOCs in tropical conditions.

In terms of interaction at the surface, the vertical profile in concentrations needs to be represented correctly to estimate the concentration at the surface that drives dry deposition. The errors caused by instantaneous vertical mixing in the lowest grid cell of an atmospheric model have been appreciated, and steps taken to adjust for the vertical profile at the sub-grid scale [O'Connor *et al.*, 2004]. However, physical processes such as deep convection are still poorly represented at a sub-grid scale in models, leading to uncertainties in the actual vertical distribution of gases such as ozone [Wild, 2007]. This has implications for all models that attempt to predict future patterns of ozone concentration and deposition in a climate where increasing intensity of deep convection are predicted.

Conclusions

Better knowledge of the future impacts of climate change on land-surface interactions would be gained by:

> Better current-day global maps of vegetation, in terms of cover and species distribution.
>
> Better estimates of future vegetation cover, taking into account changes related to economic and social pressures as well as the effects of changes in climate.
>
> Models of interactions between climate change, atmospheric change and their combined effects on BVOC emissions that take into account the possibility of adaptation and acclimation, at the plant, species and ecosystem level.
>
> Better awareness of the spatial and temporal heterogeneity of the processes being modelled.

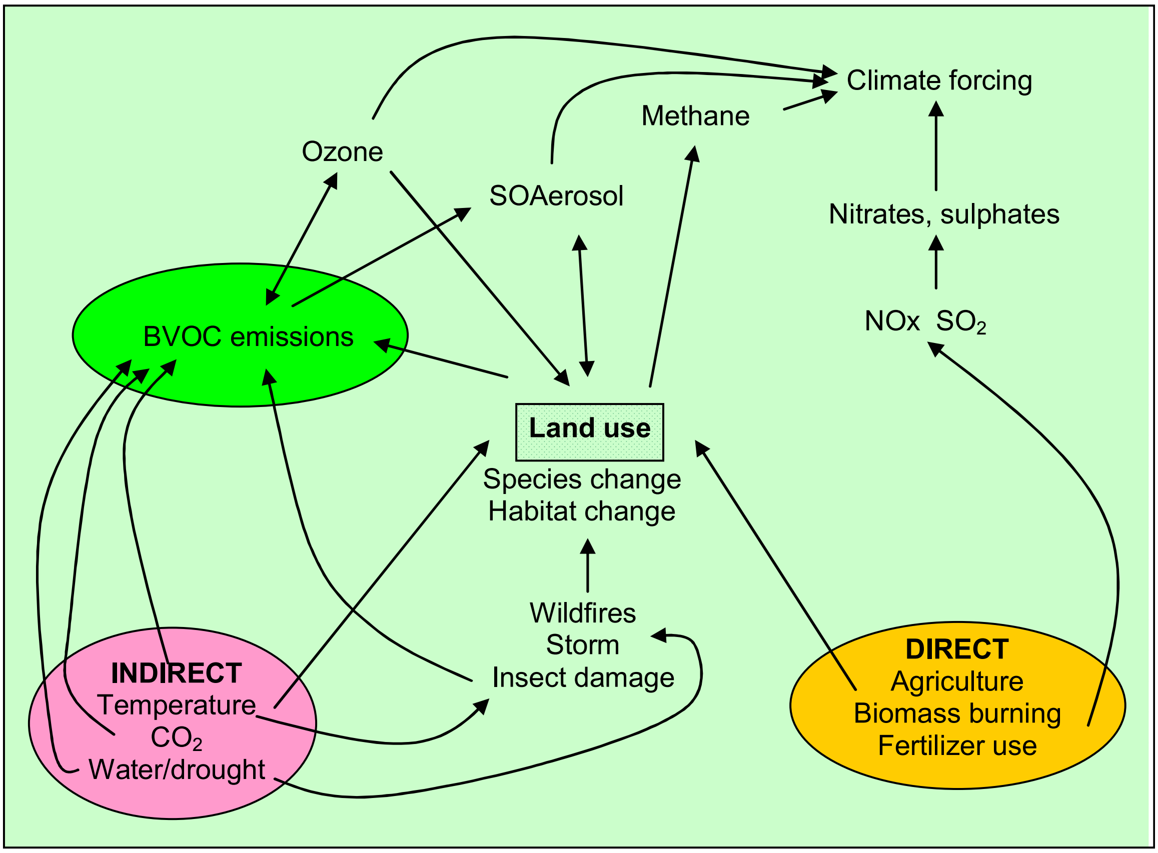

Figure 1. Schematic of processes related to climate change that have an impact on land use, and therefore on emissions of BVOC, leading to changes in atmospheric composition and chemistry.

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Modelling NO Emission from Soils on a Regional Scale

A contribution to the ACCENT CCAQ: Group 2

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Summary

NO emissions from soils might be very variable in space and time, due to the influence of such drivers as soil conditions, agricultural practices (crop, fertilisation) and climate. It is thus important to account for these influences when estimating emissions in chemistry-transport models. We propose a methodology to estimate NO emission from soil with high resolution and considering the influence of environmental and agronomic factors. It is based on the crop model CERES-EGC and the use of databases on soils, crops and agricultural practices given by the agricultural census. The meteorological database is provided by the mesoscale model MM5. The results showed the main sources of variation of NO emissions, and their sensitivity ot changing climate, as well as the complexity of interactions between environmental factors such as temperature and soil water content.

Introduction

Agricultural soils have been recognized as a significant source of nitric oxide (NO) in a large panel of scientific papers [Davidson and Kingerlee, 1997] but their contribution is still very uncertain. Moreover, they might influence significantly tropospheric ozone chemistry in rural areas, where ozone production might be limited by NO_x concentration because the NO_x emissions from combustion are smaller. In such conditions, the magnitude of NO emissions from soils, their timing relative to the period of ozone peaks and their localization at regional scale are highly required to predict ozone peaks, especially in the vicinity of urban areas.

The production of NO in soils is linked to the transformation of nitrogen in soils, mainly the nitrification and denitrification processes [Garrido *et al.*, 2002]. Nitrification is an oxidation of NH_4^+ to NO_2^- and NO_3^-, which requires aerobic conditions. Denitrification is an anaerobic reduction of NO_3^- to gaseous form of N (N_2O, N_2, NO). NO production by soil is dominated by nitrification in temperate zones. The production of NO depends on environmental and agronomic factors, including cropping practices (fertilisation, soil tillage), soils characteristics and climate sequence. The former determines the dynamic of soil ammonium content and thereby nitrification activity, while the latter influences soil temperature and water filled pore space (WFPS), which is a proximate for soil oxygen concentration and a driver for gaseous diffusion [Linn and Doran, 1984]. Soil properties, as well as agricultural activities and practices might be very variable in space at regional scale, inducing variations in NO emission fields. Moreover climate conditions and the timing of agricultural practices induce large variation with time of NO emissions [Yienger and Levy, 1995; Laville *et al.*, 2005]. This means also that changes in land use and in agricultural practices in a near future, due to climate change as well to agricultural and environmental policies might modify emissions of NO from soils and from agricultural activities as a whole. This might have consequences on the ozone level at regional scale.

The objective of this study was to develop a detailed inventory of NO emissions from soils at regional scale accounting for soil conditions and agricultural practices in order to improve NO emission in ozone prediction models and to analyze possible trends in NO emissions due to climate change or changes in agricultural practices and policy. It has been applied in the Ile de France region, where large ozone peaks occur due to NOx and VOC emissions from the anthropogenic activities.

Methods

General approach

In order to account for the influence of the main drivers on NO emission from agricultural soils, we used a crop model, CERES-EGC. This model uses as input the soils conditions, standard meteorological data and agricultural practices and delivers as output the NO fluxes, evapotranspiration and soil temperature (see Fig. 1). This requires use of different geo-referenced databases and maps available from environmental agency, agricultural census and meteorological models. Data are available at a range of time scales, from hourly data (meteorological variables), annual data (agricultural practices) and one-off data (soil types). To simulate NO emission at regional scale, CERES-EGC is run over each area for all the combinations of crops and soil conditions. Then, an average NO emission for each area is calculated by weighing according to crop and soil type density. This gives a map of NO emission for every day of the year. This map will be transformed into a grid with 1 km resolution and will serve as input to the Chemistry Transport model Chimère (http://euler.lmd.polytechnique.fr/chimere/).

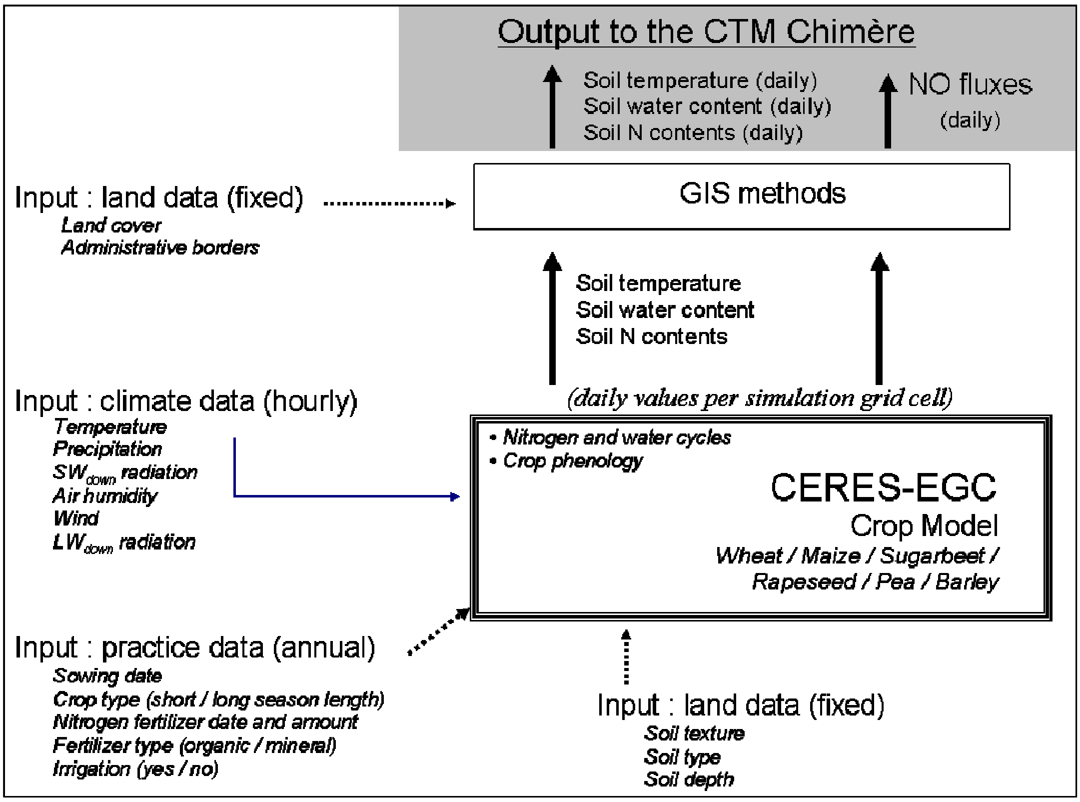

Figure 1. Diagram showing the functioning of the model

The crop model CERES-EGC

CERES-EGC was adapted from the CERES family of soil-crop models [Jones and Kiniry, 1986], with a focus on the simulation of environmental outputs such as nitrate leaching and gaseous emissions of NH_3, N_2O and NO[Gabrielle *et al.*, 2006]. CERES-EGC contains sub-models for the major processes governing cycles of water, carbon and nitrogen in the soil-crop system.

The NO *emission model*

For NO emissions, it includes the Laville *et al.* [2005] model, which simulates the production of NO in agricultural soils through the nitrification pathway. CERES-EGC predicts the driving variables of this NO production model using as input information on soil type, meteorological conditions and agricultural practices [Rolland *et al.*, 2007]. The nitrification pathway is based on Garrido *et al.* [2002] which expresses the total nitrification as the product of a potential rate with 3 functions related to soil temperature, water content and ammonium content, which are all calculated by the CERES-EGC model.

The databases

Agricultural information

Agricultural and forested areas cover 55 % and 23 % of the Ile de France region (12,072 km²), respectively. Agricultural information was available either at cantonal or department scale. There are approx. 300 cantons in the Ile de France region, and 8 departments among which 4 are almost entirely urban (Paris agglomeration).

Agricultural information was available from a service of the Ministry of Agriculture (http://www.agreste.agriculture.gouv.fr/) for areas by crops at cantonal scale and agricultural practices (sowing and fertilisation dates, average amounts of applied fertilisers) at the regional scale. The agricultural statistics showed that six crops (wheat, barley, maize, rapeseed, pea and sugar beet) and fallow soil covered 91 % of the agricultural area.

Soil database

14 soil types were derived for the Ile de France region from a 1:250,000 scale soil database produced by the INRA-InfoSol service (http://www.orleans.inra.fr/les_unites/us_infosol). The database was organized into geographical soil map units (SMU), based on main soil types and hydraulic characteristics.

Climate data

CERES-EGC requires solar radiation, minimum and maximum temperature at screen level, rainfall and evapo-transpiration. To derive those data at hourly timescale on a 5 km grid, the NCAR meso-scale model MM5 was used with a two-nesting procedure for the Ile de France domain. Hourly values were then converted to daily values as input to CERES-EGC. The evapo-transpiration was calculated from the daily values with the Penman equation.

Results

Time variations of NO *emissions*

Figure 2 shows the NO emission calculated by CERES-EGC for two crops (winter wheat and maize) and one set of soil and meteorological conditions, using the standard agricultural practices provided by the agricultural census. The crops were chosen to give the main variation in NO emission timing and range: wheat is a winter crop, sown in

October, fertilized in March and April and harvested in July, while maize is a spring crop, sown and fertilized in April/May and harvested in October.

It can be seen in Figure 2 that the timing of NO emission is tightly linked to fertilizer application. Emissions lasted 2-3 months after that period, and they are almost negligible (several g/ha/day) during the rest of the year. Moreover, NO emissions over the maize crop were approx. 50 % larger than over wheat: the cumulated emission over maize and wheat amounted to 6793 g/ha and 4439 g/ha over one year. This is certainly mainly due to the effect of temperature, as fertilizers are applied later, and thus in a warmer period over maize than over wheat (the amount of fertilizer was slightly larger over wheat than over maize).

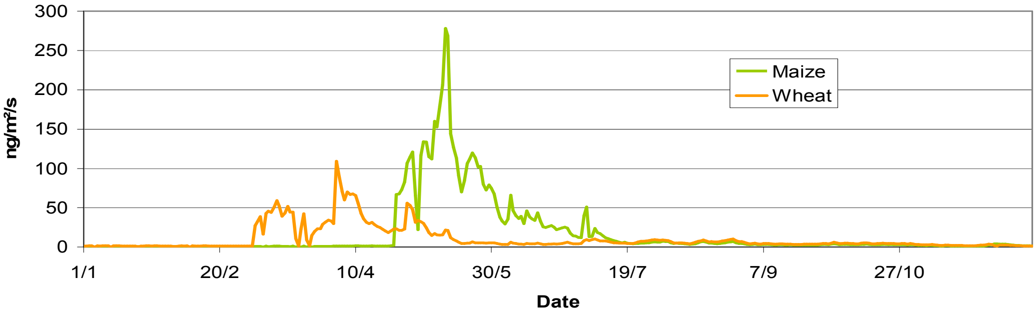

Figure 2. NO fluxes estimated by the CERES-EGC model for two crops, winter wheat (orange) and maize (green) for the year 2001.

Spatial variation in NO *emissions*

Figure 3 shows maps of cumulated NO emission from either wheat or maize crop over a 17 months period. This confirms larger emissions over maize, compared to wheat. A large heterogeneity in NO emission can be observed on both maps, with a range of 6 to 13 kg of NO per ha for maize and 3 to 6 kg for winter wheat, estimated over the 90 % most emitting SMUs. In both cases largest emissions are observed in the same zones: in the East of Paris and, to a lesser extent in the South and South-West.

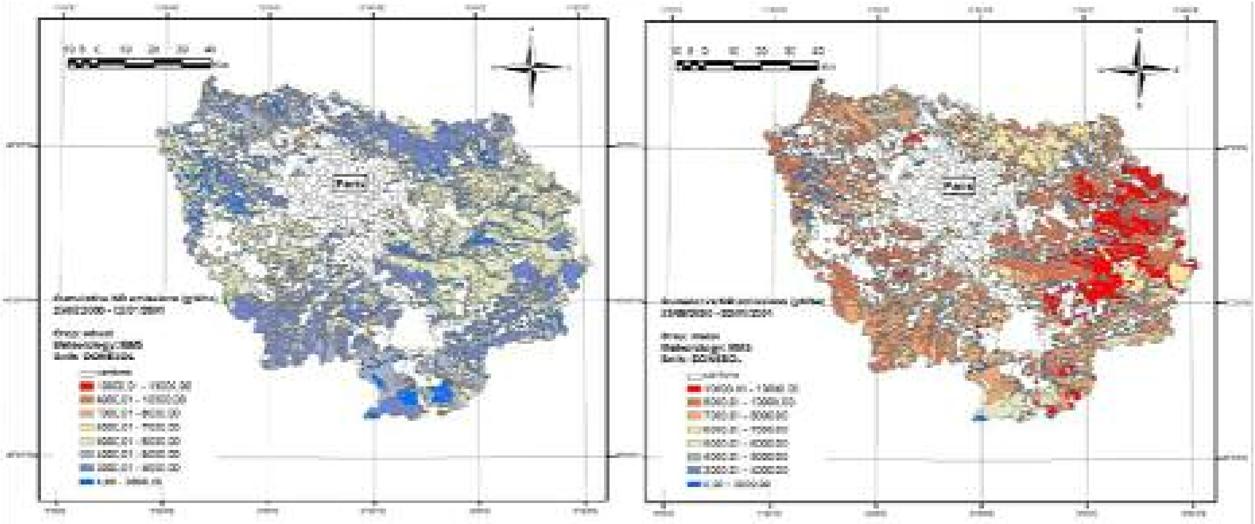

Figure 3. Cumulated NO emissions (in g/ha) for wheat (left) and maize (right) crop from August 1st 2000 to December 31st, 2001 over the Ile de France region. The homogeneous units are soil map units, corresponding to one soil type used in CERES-EGC. White units correspond to non agricultural soil, either forest soils or urban zones.

This corresponds mostly to the distribution of soils at regional scale. The largest emitters correspond to luvisols. Analyses using either the model with a unique soil and a changing meteorology or a unique meteorology and the soil map, confirmed that the soil conditions were a major driver of NO emissions. Moreover, a sensitivity study was performed on soil properties, crop types (including fertilization practices) and climate. It showed that the calculated emission were sensitive, by decreasing order, to soil type, crop type and climate.

Changes in NO *emissions in a warmer climate*

A very simple scenario was applied to our dataset. An increase in input air temperature of 2 °C was applied all over the year and at any time of the day. The relative variations in NO emissions shown on Figure 4 show that the response is very different for the two crops. An increase of 5-20 % was observed for the wheat crop, with the largest increase in the zones where large emissions occurred (East and West of Paris). In contrast, a decrease between 2 and 5 % was observed for most cases over maize. The decrease was the largest in the places where the emissions were the largest. In the case of wheat, the increase might be due to a temperature effect, while the decrease observed over maize might be due to a limitation due to water availability as a consequence of increased temperature.

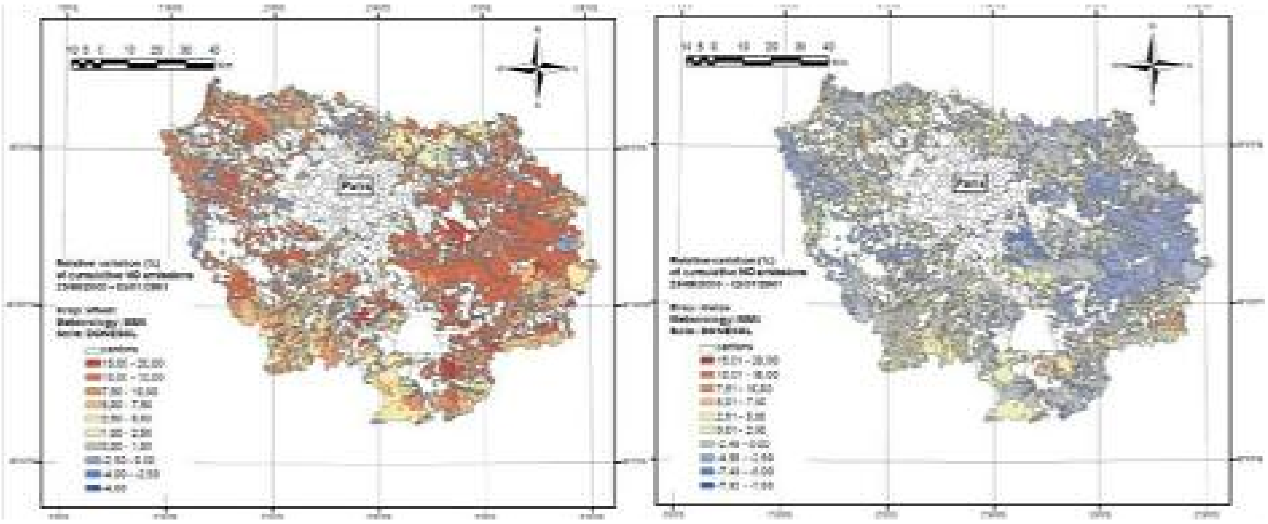

Figure 4. Relative changes in cumulated emissions shown in Fig. 3 for a 2°C increase in temperature

Conclusions

This approach highlighted the need to consider local characteristics such as soil type, crop type, agricultural practices and climate for estimating spatial and temporal variations in NO emission from soils. This might be of particular importance when agricultural areas are close to large urban areas where significant ozone production occurs in summer. This is the context of many large towns and many productive agricultural regions. As drier summer and earlier ozone peaks are expected, the pattern of NO emission might change in the next decades and the consequence on ozone concentrations should be considered. Then, accounting for time variation in NO emission will be especially important to provide realistic NO emissions in ozone prediction models during ozone peak episodes. This requires a model able to account for the main drivers of NO emissions, *i.e.* soil and crop type, agricultural practices and meteorological conditions. Moreover the input data must be available. This should not be a problem in most European countries, where soil maps are available, as well as agricultural statistics (crops, practices, fertilization) and high resolution meteorological data. The next step is to provide a CTM model with these NO emission varying in space and time to assess their impact on ozone peaks at regional scale.

This study also showed the complexity of interactions between environmental (soil, climate) and agronomic factors (crops, fertilization practices) and the need to account for these to analyse the effect of changing practices or changing climate on NO emissions. As a matter of fact, changing crops from *e.g.* spring crops to winter crops, following possible milder winters, might change NO emissions strength as well as emission patterns. Then, assessing the impact of climate change on NO emission also needs to consider changes in land use, choice and change in cropping systems and agricultural practices.

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Effects of Changing Temperature on Leaf Surface Water-Film Chemistry and Trace Gas Exchange Processes over Terrestrial Vegetation

A contribution to ACCENT CCAQ: Topic 2

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Summary

The potential effect of changing temperature on leaf surface water chemistry and trace gas exchange with the atmosphere is investigated from a theoretical viewpoint and using a dynamic chemical compensation point model applied to measured field data. The canopy resistance for SO_2 is expected to increase by 5-20 s m^{-1}, but the effect on R_cNH_3 is likely to be only of the order of 1-5 s m^{-1}, except where the NH_3 concentration is high, or where SO_2 oxidants are limiting. In dry conditions stomatal exchange becomes dominant, and stomatal compensation points for NH_3 would increase by +20-50 %, but the change in stomatal conductance is more uncertain, depending on land use and geographical location.

Introduction

The dry deposition of atmospheric trace gases to terrestrial vegetation is currently modelled in national or regional atmospheric transport models using canopy resistance (R_c) or canopy compensation point (χ_c) schemes [Smith *et al.*, 2000; Simpson *et al.*, 2003]. Both R_c and χ_c models require the quantification of a cuticular resistance (R_w or R_{ext}) to account for chemically-driven exchange processes occurring on the non-stomatal leaf surface [Sutton *et al.*, 1998]. The presence of water films or droplets caused by rain, dew, guttation or even deliquescing salts, is especially important for water-soluble trace gases such as NH_3 and SO_2, creating marked dynamics in exchange patterns with frequent wetting events and subsequent evaporation, so that R_w can be hysteresis-dependent [Flechard *et al.*, 1999].

The parameterizations for R_w that have been suggested over the years [Nemitz *et al.*, 2001, for a review], and implemented in European regional modelling studies [Smith *et al.*, 2000; Simpson *et al.*, 2003], are mostly based on relative humidity (RH) or vapour pressure deficit (VPD). These empirical schemes, derived from past field studies, do not address explicitly and mechanistically the combined effects of ambient temperature on solubility in water, solute dissociation equilibria and aqueous or heterogeneous reactions, such as SO_2 oxidation to SO_4^{2-}. This contribution seeks to estimate the extent to which a regional warming of a few K may shift the biosphere/atmosphere partitioning of gaseous pollutants.

Theoretical considerations

Trace gas solubility in water is given by the temperature-dependent *effective* Henry coefficient (K_h*), that results from the combination of the actual Henry coefficient K_h with the dissociation constant(s) of the hydrated molecule in water [Seinfeld and Pandis, 2006]. For NH_3 and SO_2, the ratio of dissolved + dissociated aqueous concentration to the partial pressure in air decreases with increasing temperature (at constant pH).

Figure 1a shows that the reduction in effective solubility even for a small temperature change (δT) of +1 to +5 K is significant, 10-50 % for NH_3, and 5-30 % for SO_2. Thus, at terrestrial sites where vegetation is wet typically half the time over the course of one year, the sink strength of water films for atmospheric gases should theoretically decrease. In sub-stomatal cavities and in the mesophyll where extra-cellular water is present the same theoretical effect should apply, and indeed K_h* has been suggested [Wesely *et al.*, 1989] as a scaling factor for mesophyll resistance. By the same mechanism, the NH_3 apoplastic compensation point rises exponentially with temperature [Sutton *et al.*, 1998].

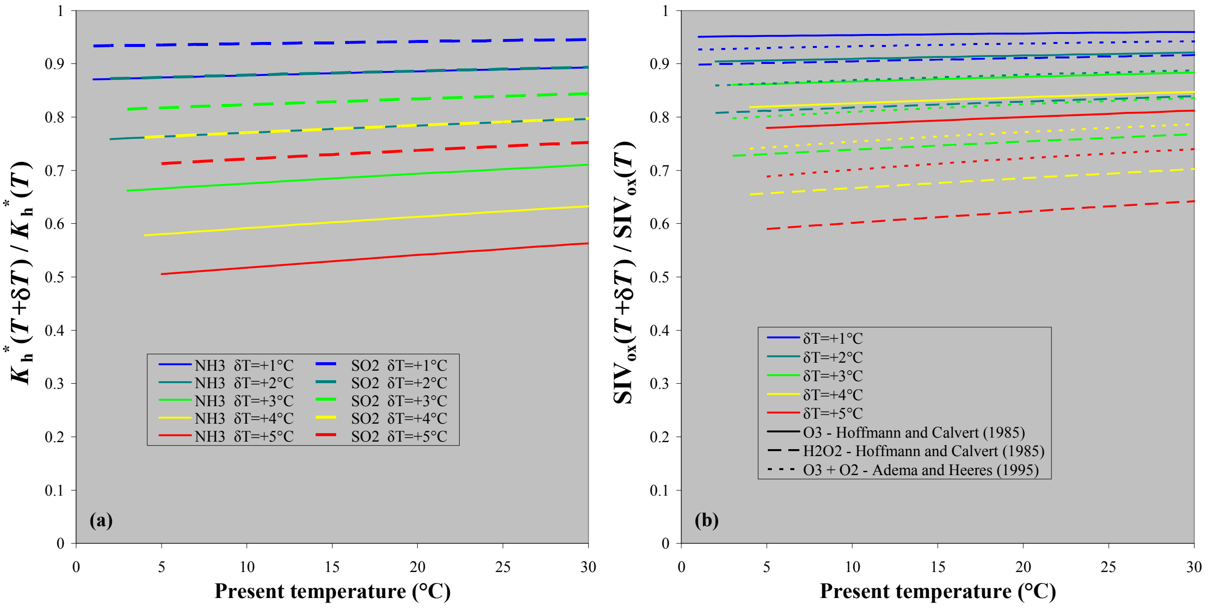

Figure 1. Left: Reduction in effective solubility due to a temperature rise of a few K, expressed by the ratio $K_h*(T+\delta T)$ / K_h $*(T)$. Right: Reduction in the *bulk* sulfur dioxide oxidation rate, expressed by the ratio $SIV_{ox}(T+\delta T)$ / $SIV_{ox}(T)$, at pH = 5 and with ambient O_3 and H_2O_2 concentrations of 25 ppb and 0.5 ppb, respectively.

Conversely, following the Arrhenius equation $k(T) = A*\exp(-E_a/RT)$ and since the activation energy E_a is positive, the rates of chemical reactions such as the heterogeneous SO_2 oxidation on wet leaf surfaces will increase with increasing temperature. This would tend to increase the sink strength of surface wetness by lowering the aqueous concentration of the dissolved gas. The relative importance of the temperature effects on solubility ($dK_h*/dT < 0$) and on chemical reactions ($dk/dT > 0$) determines the overall net impact on the sink strength. For SO_2, using oxidation rates by O_3, O_2 or H_2O_2 from the literature, it can be shown (Figure 1 right) that the *bulk* conversion rate of S(IV) to S(VI) (expressed in mol l^{-1} s^{-1}) actually decreases with increasing T, as the faster reaction (*per mole*) cannot compensate for the Henry-induced decline in dissolved reactant (SIV, O_3, H_2O_2) concentrations. This, however, is only true at constant pH. To address the issue, a dynamic chemical modelling of surface wetness is required that takes multiple influences mechanistically into account.

Theoretical kinetics of a thin water film

In the simplest case, building on the study by Cape [1996], a theoretical 0.1mm-thin water film of constant thickness (no evaporation) is considered, with constant turbulent (R_a) and laminar viscous sub-layer (R_b) transfer resistances and $R_a + R_b = 100$ s m^{-1}, so that the maximum deposition velocity allowed is $V_{d,max}$=10 mm s^{-1}.

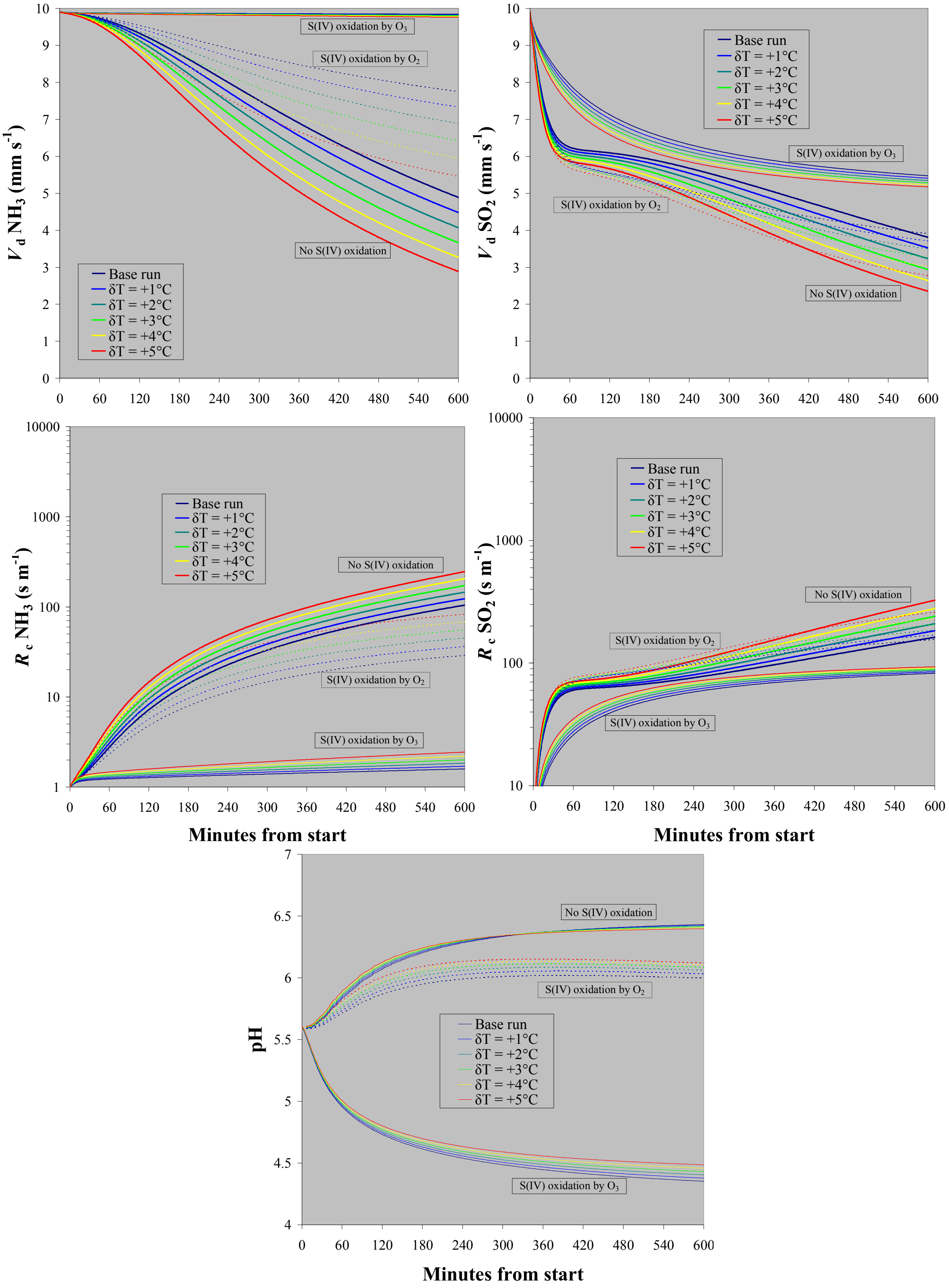

Figure 2. Simulation of NH$_3$ and SO$_2$ uptake (V_d: deposition velocity; R_c: canopy resistance) by a theoretical 0.1mm-thin water film, and time course of pH. The base run was calculated for a temperature of 10 °C. Air concentrations in this simulation are 1 ppb NH$_3$, 1 ppb SO$_2$ and 25 ppb O$_3$.

At t = 0, this is a pure solution in equilibrium with an atmospheric CO_2 mixing ratio of 380 ppm, with pH = 5.6 at 10 °C. Constant NH_3 and SO_2 concentrations are maintained in the air above the water film, and three scenarios are considered: 1 ppb NH_3 and 1 ppb SO_2 (Figure 2); 5 ppb NH_3 and 1ppb SO_2; 1 ppb NH_3 and 5 ppb SO_2. Sulfur oxidation in the liquid phase is simulated using the scheme by Adema and Heeres (1995) with heterogeneous oxidation by 25 ppb O_3 or by molecular oxygen (uncatalyzed) (Figure 2), but the "no oxidation" case is also displayed for comparison.

The data [Cape, 1996] show that in the absence of chemical reactions (irreversible sinks) both NH_3 and SO_2 accumulate in the water film and dry deposition is self-limiting over time, as both R_c (defined as $1/V_d - R_a - R_b$) and pH keep rising. In this theoretical case of a thin water film, with none of the other potential sinks or sources found in a vegetation canopy, R_c may be considered as the equivalent of R_w. With a fast S(IV) oxidation by O_3, as predicted by the Adema and Heeres [1995] parameterization, SO_2 saturation does not occur as R_cSO_2 stabilizes around 80-100 s m^{-1} and, as pH drops below 4.5, R_cNH_3 remains negligible (a few s m^{-1}).

The effect of a 5 K temperature increase on R_c is marked when SO_2 oxidation is absent: 5 hours after t0, R_cNH_3 is 33 s m^{-1} for the base run (10 °C) but 71 s m^{-1} at 10 + 5 = 15 °C; at the same time R_cSO_2 is 85 s m^{-1} at 10 °C but 128 s m^{-1} at 15 °C. Conversely, the same temperature increase has practically no effect on R_cNH_3 if SO_2 oxidation by O_3 is active (from 1 to 2 s m^{-1}), but there is still a significant increase of R_cSO_2 from 66 s m^{-1} to 76 s m^{-1}. Field reality probably lies somewhere between the two extremes, as higher atmospheric O_3 concentrations (and those of other oxidants such as H_2O_2) are generally associated with warm and dry conditions, while lower levels are expected on rainy days and during night-time, when leaf surfaces are wet from dew or precipitation. The mean effect of a general temperature rise will depend on water film thickness and the daily variations thereof (and on changing precipitation patterns), while the availability of oxidants is expected to be critical in areas where SO_2 concentrations are high.

The three scenarios with different NH_3 and SO_2 mixing ratios are summarized in Figure 3. In all three cases, the impact of a temperature change on R_c (as taken 5 hours after t_0) for both gases is lowest when SO_2 oxidation is active and fast, but even then there can be a significant effect on R_cSO_2 if the atmospheric NH_3/SO_2 molar ratio (N/S) is much lower than 1, and an effect on R_cNH_3 is N/S is much greater than 1. For surface acidity, $d(pH)/dT < 0$ for high N/S values and $d(pH)/dT > 0$ for low N/S.

Application of a dynamic chemical compensation point model to field data

To assess the potential effect of changing temperature on the mean sink or source strength for NH_3 and SO_2 in field conditions, with dynamically-varying water layer thickness, surface wash-off by falling rain, changing atmospheric concentrations of other gaseous pollutants (HNO_3, HONO, HCl), and seasonal variations in the phenology of the underlying canopy, a dynamic leaf surface chemistry, canopy compensation point model [Flechard *et al.*, 1999] was used. A constant offset of $\delta T = +1$ to +5 K was added to monitored ambient temperature, for comparison with the base run, as the model was applied to long-term monitoring fluxes from a semi-natural, moorland site at Auchencorth Moss, UK, 1995 to 1996 [Flechard *et al.*, 1999].

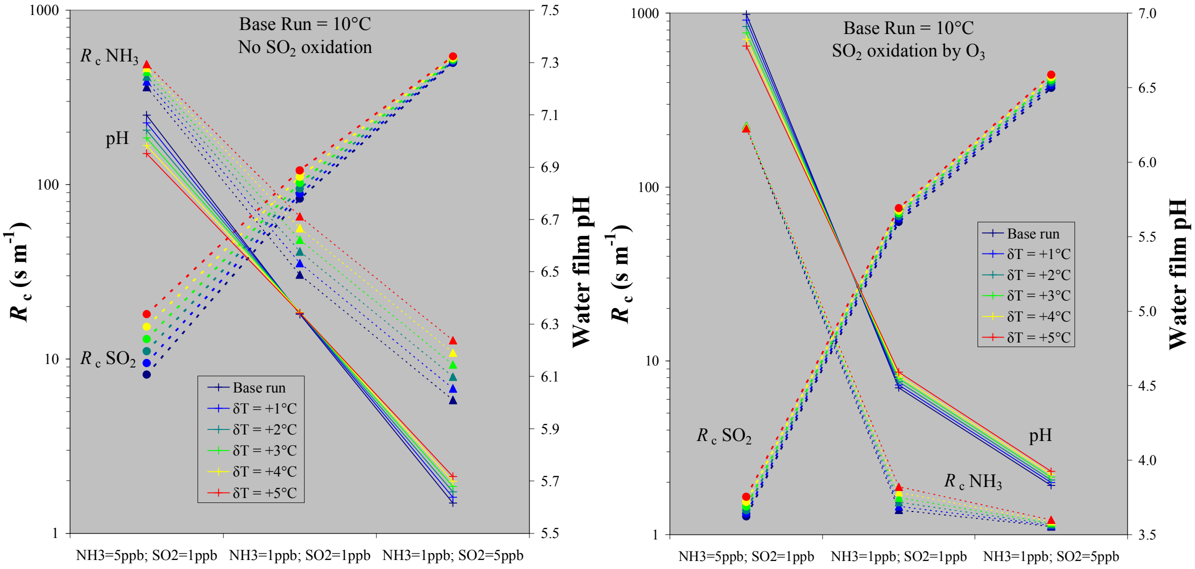

Figure 3. Simulated influence of temperature change and NH_3 and SO_2 mixing ratios on canopy resistance (R_c) and pH for a theoretical 0.1mm-thin surface water film.

The two-leg, single-layer model output is of total (F_t) surface/atmosphere NH_3 and SO_2 flux, as well as its components the stomatal (F_s) and cuticular (F_d) fluxes, driven by the modelled water-film and equilibrium air concentrations χ_d, and by the stomatal- and canopy compensation points χ_s and χ_c (Figure 4 left). From these data, an *effective* R_w may be derived assuming that $\chi_d=0$, which is the standard assumption in conventional (static) R_c or χ_c models [Smith *et al.*, 2000], such that:

$$R_w = \frac{-\chi_c}{F_d} \tag{1}$$

R_w can only be calculated if $F_d < 0$ (deposition case), but since deposition to the cuticle dominates, with only occasional desorption fluxes when the cuticle dries out [Flechard *et al.*, 1999], the mean F_d is negative, so that a mean (annual) effective R_w can be obtained from mean modelled χ_c and F_d. (Figure 4 right). Similarly, a mean effective R_c may be derived for the whole canopy, assuming a zero surface concentration, if, as in the case of this semi-natural ecosystem, deposition prevails for both NH_3 and SO_2. Note that in the dynamic model, the simulation of wet chemistry was limited to time intervals when the water layer was deep enough such that the solution ionic strength was less than a threshold of 0.3 M, with the consequence that the mean R_w presented here is representative of wet conditions only.

As expected, all equilibrium concentrations, compensation points and surface resistances increase with temperature (Figure 4). However, the increase in effective R_w or R_c is only significant for SO_2, of the order of +4 s m^{-1} K^{-1}, and is a consequence of a reduction of 3.3 % K^{-1} of the effective S(IV) oxidation capacity. Mean leaf wetness pH is around 4.5 and remains relatively unaffected by a temperature rise at this site (data not shown), which is why R_wNH_3 is also constant over the range of temperature change studied. By contrast, there is a near doubling of the mean stomatal NH_3 compensation point, from a current 0.077 µg m^{-3} up to 0.144 µg m^{-3}. A change in stomatal resistance is also expected to occur as temperatures move toward, or away from, the optimum temperature for plant growth [Jarvis, 1976].

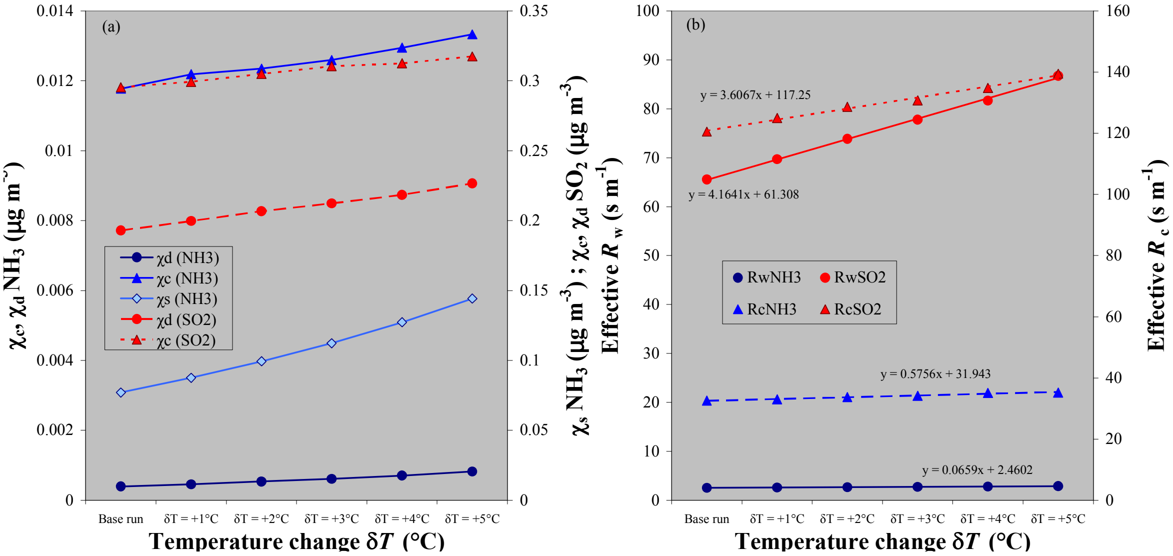

Figure 4. Simulated influence of temperature change on mean annual vegetation/atmosphere exchange parameters for wet conditions at Auchencorth Moss moorland. (a): cuticular- χ_d , stomatal- χ_s and canopy χ_c compensation points; (b): effective mean R_w and R_c values derived from modelled fluxes.

For northern European ecosystems, where low temperatures currently limit stomatal conductance and plant growth, a regional warming of a few K could theoretically result in an increase of stomatal conductance by 10-30 %, though this may be offset by the effect of increasing atmospheric CO_2 concentration. The effect would be enhanced by a lengthening of the growing season and reduction of snow cover. Conversely, in Mediterranean ecosystems, the same warming could result in reduced stomatal conductance by a comparable amount, which may be compounded by increased frequency and severity of droughts, and by the impact of elevated O_3 concentrations and foliar injury.

Conclusions

The parameterizations for non-stomatal leaf surface resistance to dry deposition (R_w) currently used in European dry deposition models for *e.g.* SO_2 and NH_3 either use a binary wetness indicator, or a functional dependence on ambient relative humidity across the whole humidity range, but they ignore the effect of ambient temperature on superficial leaf wetness chemistry. Model simulations show that an increase in mean temperature by as little as +1 to +5 K may lead to a significant rise in canopy resistance for soluble gases and alter their vegetation/atmosphere partitioning. The R_w schemes within R_c or χ_c models would need to be revised accordingly in order to predict the overall effect of regional or global warming on both air quality and atmospheric deposition inputs. Plant stomatal compensation points for NH_3 are expected to rise and lead to reduced NH_3 deposition. Modelling efforts also need to take into account changes in precipitation frequency and intensity, which are more difficult to predict, as well as changes in land use, vegetation and atmospheric composition.

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Changes of Stomatal Conductance and Ozone Uptake in *Fagus sylvatica* with Changing Air Temperature: Results from a Simulation

A contribution to ACCENT CCAQ: Group 2

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Summary

The effects of an increase of air temperature on the stomatal conductance of beech, a widespread tree specie in Europe, have been examined by using a Jarvisian model of stomatal conductance calibrated on a sixth months long field experiment in northern Italy. An increase of few degrees centigrade in air temperature resulted in very little changes in the mean stomatal conductance of the trees, but the diurnal course of this important parameter underwent an evident change, consisting in increased stomatal conductance values in the first hours of the day and decreased values in the rest of the day, and particularly in the afternoon.

Introduction

The stomatal conductance is the way through which the plants regulate the gaseous exchanges with atmosphere. The exchanging characteristics of any vegetated surface is strongly affected by the behaviour of the stomatal conductance, g. This important parameter is under physiological control and responds to environmental conditions such as light, air temperature, vapour pressed deficit, soil moisture and wind speed. The stomatal behaviour have been conveniently modelled by Jarvis [1976] though a multiplicative approach which involves the maximum expressible stomatal conductance by plant in optimal condition, g_{max}, and a series of functions f, whose value is ranging between 0 and 1, describing the limitation effect played by the different environmental parameters on the stomatal conductance:

$$g = g_{max} \cdot f_{Light}(PAR) \cdot f_{Temp}(T) \cdot f_{VPD}(VPD) \cdot f_{SMD}(SMD) \cdot \ldots$$

where PAR represents the photosynthetically active radiation, T the air temperature, VPD the vapour pressure deficit and SMD the soil moisture deficit.

Once calibrated, the model might be employed to predict the stomatal conductance from the environmental parameter only [Emberson *et al.*, 2000].

In this work a stomatal conductance model calibrated for *Fagus sylvatica* in Northern Italy environmental condition have been used to examine the possible role of changing air temperature on the stomatal conductance to water vapour, g_w, and ozone removal by plants' stomata, AFst0, in a whole vegetative season (1st April – 30th September).

Activities

In order to test the effects of a change in air temperature on stomatal conductance a dataset of measurements on a European widespread tree specie was considered. The dataset refers to an experiment aimed to evaluate the effects of ozone fluxes on young beech trees grown in open plots and open-top chambers at Curno (Lat. 45.700 °N, Long. 9.620 °E, elev. 242 m a.s.l.), northern Italy. A group of trees was subject to continuous water supply for the whole growing season (“wet”) and another group was exposed to the water naturally received by rain (“dry”). In this context a Jarvisian model of stomatal conductance was calibrated and validated against leaf conductance measurements by means of portable porometers. Details are reported in Gerosa *et al.* [2007] and the *f* function f_{PAR}, f_T, f_{VPD} and f_{SMD} are resumed in Figure 1. The 2005 dataset (1st April-30th September) of climatic and environmental parameters of the group of trees grown in open plots and exposed to normal rainfall was selected to perform by 1 and 2 °C with respect to the temperature actually recorded in the semester 2005, and the stomatal conductance to water vapour, g_w, and the cumulated stomatal flux of ozone, *AFst0,* were recorded; all the other parameters were left unchanged. This is, of course, an important simplification because it is well known that an increase in temperature is accompanied by a decrease in air relative humidity, rainfalls and soil moisture deficit due to an increased evaporation.

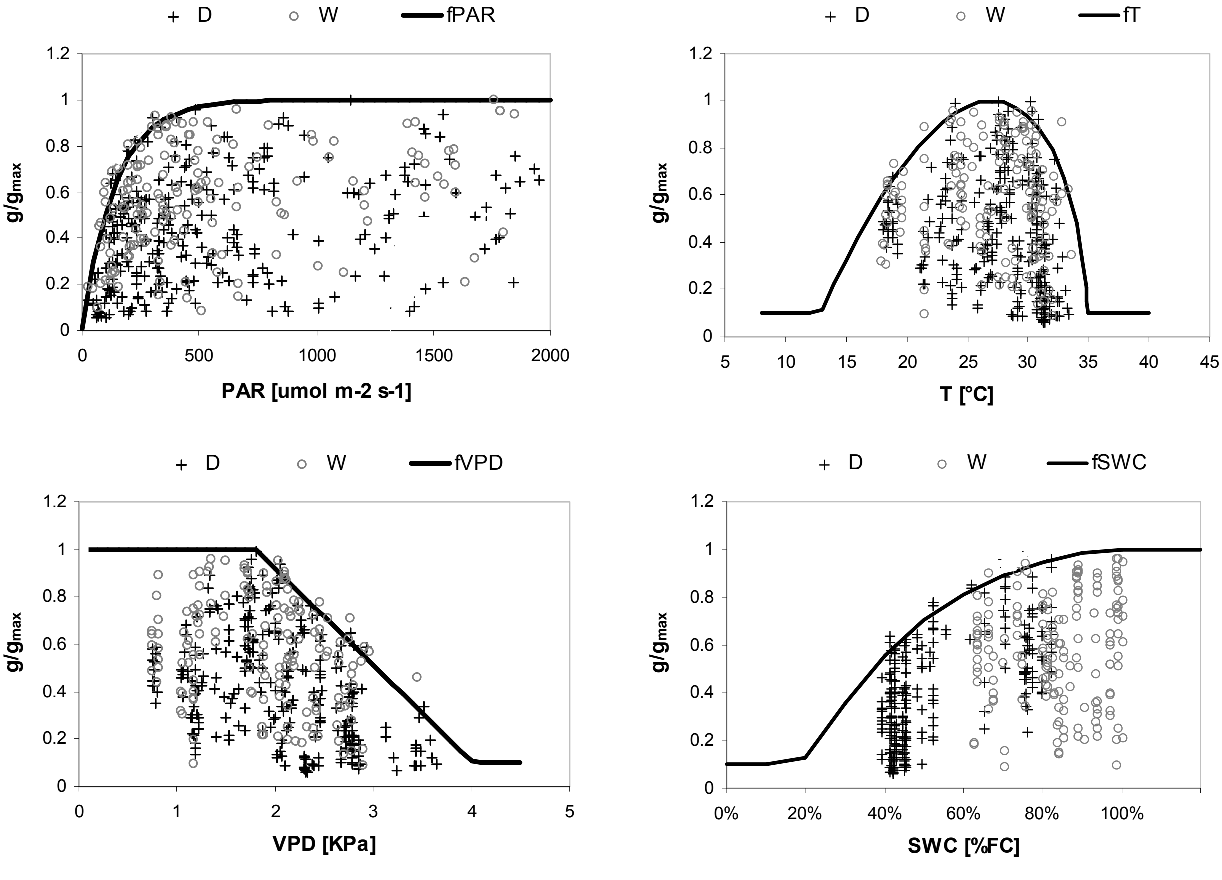

Figure 1. *f* functions for the Jarvisian stomatal conductance model of *Fagus sylvatica*. D, non-irrigated plants; W, irrigated plants; *PAR*, photosynthetically active radiation; *T*, temperature; *VPD*, vapour pressure deficit; *SWC*, soil water content; *% FC*, fraction of soil water content with respect to the field capacity; *g*, stomatal conductance; $g_{\max}$, maximum stomatal conductance.

Results and discussion

The main climatic conditions of the summer 2005 at Curno, assumed as reference in this study, are summarised in Table 1. The effects of an increase of few degree centigrade of air temperature on the mean stomatal conductance of beech trees in the whole vegetative semester is reported in Table 2. It can be observed that an increase of air temperature up to 2 °C results in a very little change in g_w. Only a significant increase of

5 °C of the air temperature causes a 10.8 % reduction of the average stomatal conductance. Much sensitive to a temperature change appears the total amount of ozone removed by the trees' stomata. Just at an increase of 1 °C the ozone removal records a decline of 2.9 %, reaching a 25.9 % reduction when temperature increases of 5 °C.

Table 1. Climatic parameters and ozone in the 2005 growing season. *O_3max*, maximum ozone concentration recorded; *T*, temperature.

	2005				
	T max	T min	O_3 max	Rain (dry Plots)	Rain (wet Plots)
Units	°C	°C	ppb	mm	mm
April	24.5	5.7	80	118	118
May	31.8	9.7	146	60	138
June	35	10.7	135	52	181
July	34.2	14.2	118	91	172

Table 2. Changes of the mean stomatal conductance to water vapour, g_w, and total ozone removed by stomata, *AFst0*, with changing air temperature. Percentages are referred to the values in the T+0 column.

T	[°C]	T-2	T-1	T+0	T+1	T+2	T+5
g_w	[cm/s]	0.268	0.277	0.282	0.283	0.280	0.251
	%	95.2 %	98.2 %	100 %	100.4 %	99.5 %	89.2 %
AFst0	[mmol m^{-2} PLA]	46.0	46.0	45.4	44.1	42.2	33.6
	%	101.4 %	101.4 %	100 %	97.1 %	92.9 %	74.1 %

But the negligible effects on the mean stomatal conductance are accompanied by evident changes in the diurnal course of this important parameter (Figure 2). These effects consist in increased stomatal conductance values in the first hours of the day and decreased values in the rest of the day, and particularly in the afternoon. Evidently the increased temperature stimulates the prompt stomatal opening in the first hours of the morning, while it triggers the stomatal closures in the afternoon, also through an increased VPD.

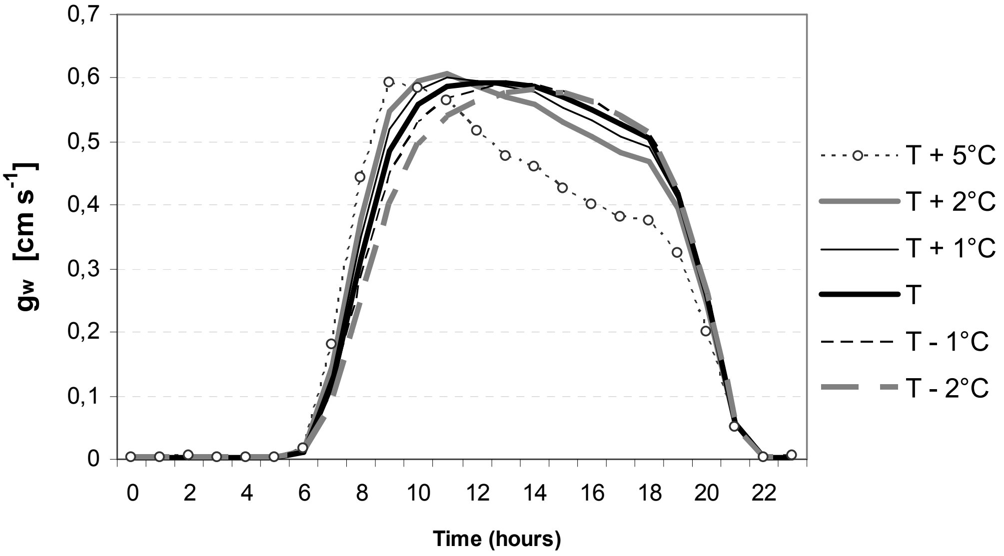

Figure 2. Changes of the mean daily course of the stomatal conductance to water, g_w, with changing air temperature during the whole vegetative semester.

In any case the effect of an increased air temperature on stomatal conductance and ozone removal is not linear as the temperature contemporarily affects the VPD, resulting in a joint action these two parameters.

Moreover the reported reduction of g_w and *AFst0* in Northern Italy are likely to be underestimated because in this area an increase in air temperature is expected to be accompanied by a decrease in rainfalls and water availability in the soil, all factors affecting negatively the stomatal opening.

Future outlook

A decrease of stomatal conductance and ozone sink capability by forest trees should be expected as a consequence of an increase of air temperature. If this lead to a better protection of the trees by photooxidants, these changes in vegetation-atmosphere interactions may imply an increased risk for human health by increased ozone levels.

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Climate Change and Land Use Interactions: The Role of Critical Thresholds and Feedbacks

A Contribution to ACCENT CCAQ: Group 2

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An issue in climate is feedbacks. The fact that the western Mediterranean Basin (WMB) is a deep sea surrounded by mountains in the subtropical latitudes makes it an ideal test ground for checking whether or not vegetation is a passive component of climate, for determining its role in drought, desertification, and for investigating air quality questions related to feedbacks in climate studies. Around the Mediterranean, deserts and desert-like conditions are found in close proximity to a warm sea and, thus, to a marine air mass with a high moisture content, *e.g.* the coasts of Algiers, Tunisia, Libya, and in south-eastern Spain. The question is: did these areas run a feedback cycle towards drought and desertification as a consequence of removing the forests and desiccating the coastal marshes? The experimental data and modelling results from several European research projects suggest that this could be the case. One result of these projects was the disaggregation of precipitation components from: (1) summer storms driven by sea breezes, (2) "classic" Atlantic frontal precipitation and (3) Mediterranean cyclogenesis. All of these, it should be strongly emphasized, respond differently to known climatic indexes, e.g. the NAO [Millán *et al.* 2005a].

In the western Mediterranean the interaction between marine air masses, land surface (heat and moisture exchanges), and atmospheric pollution (aerosols affecting nucleation), within the sea-breeze circulations can work as a threshold-dominated system. In this system, modest changes in land use and/or air pollution emissions along the coastal areas can change the properties of the air masses and modify the summer storm regime inland. The critical threshold is the height of the Cloud Condensation Level (CCL) of the air mass within the breeze with respect to the height of the coastal mountain ranges [Millán *et al.* 2005b]. If exceeded, the probability of the storm developing and maturing greatly decreases. Loss of storms results in drier soil inland, increased surface heating, and even higher Cloud Condensation Levels (CCL), all of which reinforce a feedback loop towards desertification in these areas. Loss of storms now prevails in the WMB where the return flows of the sea breezes aloft, and their compensatory subsidence over the sea become self-organized in closed vertical recirculations, that extend to the whole basin from April to early October [Millán *et al.*, 1997; Gangoiti *et al.*, 2001].

This situation affects the coasts of northern Africa, the Iberian peninsula, southern France and southern Italy, and suggests that land use perturbations accumulated over historical time [Bölle 2003], and accelerated in the last 30 years, may have induced changes from an open monsoon-type rain regime in the past, with frequent summer storms over the coastal mountains, to one now dominated by closed vertical recirculations and fewer storms. In the current situation the non-precipitated water vapour and the air pollutants then follows the return flows of the breezes aloft and accumulates over the sea. In this process a moist, polluted and increasingly unstable air mass is created over the sea. During this period, the water vapour and various secondary pollutants like ozone, with higher greenhouse properties than CO_2, act as greenhouse gases, inhibit radiative cooling of the sea and favour an increase in the sea surface temperature (SST) by the end of the summer.

Higher sea surface temperatures (SSTs) increase torrential precipitations over the coastal areas in autumn-winter [Pastor *et al.* 2001]. Because warm water pools move within the basin, they can feed torrential rains and flash floods anywhere in basin. This loop would tend to propagate the effects of land-use perturbations, including some desertification mechanisms, from one part of the basin to other parts of the basin with a three-to-six-month delay.

The cycle of storm loss and layer accumulation over the sea can persist from 3 to 10 days, *i.e.* until the air mass becomes uplifted by a travelling depression or a trough of cold air aloft. The uplifted air mass can then feed onto a V_b depression track and contribute to intense summer precipitations in central and eastern Europe [Ulbrich *et al.* 2003]. Alternatively, it can be advected along the southern Atlas corridor and/or towards central Africa, mixing with and modifying the physico-chemical characteristics of the Saharan dust transported across the central Atlantic towards the Caribbean [Prospero and Lamb, 2003, Gangoiti *et al.* 2006].

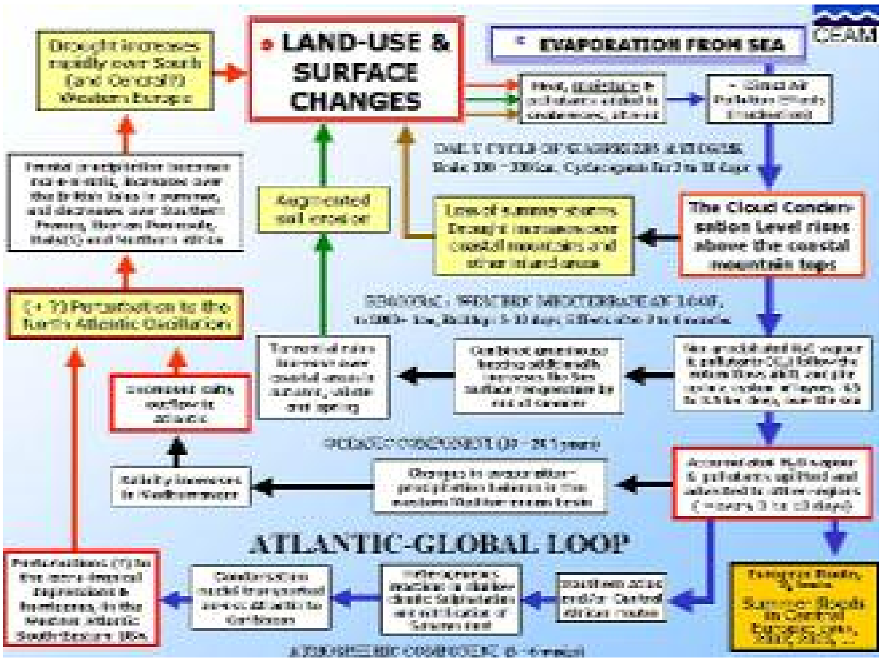

Figure 1. Feedback loops between land-use perturbations in the western Mediterranean basin and the climatic-hydrological system from the local through the regional to the global scales. The first, local, loop involves the sea breezes and the storms that develop in the afternoon over the coastal mountain ranges. The regional loop influences the evolution of the sea surface temperature in the western basin during the summer. This warm(er) water then feeds torrential rains in the autumn, and more recently also in winter and spring. Finally, the Atlantic-global loop has two components which can affect the North Atlantic Oscillation (NAO): the output of saltier water to the Atlantic and the possible perturbations to the extra-tropical depressions and hurricanes in the Gulf of Mexico generated by changing the characteristics of the Saharan dust transported across the Atlantic. In this figure the path of the water vapour is marked by dark blue arrows, the directly related effects by black arrows, and the indirect effects by other colours. Critical thresholds are squared in red [Millán, 2007].

Finally, the loss of the moisture accumulated over the sea (non-precipitated in the local storms) alters the evaporation-precipitation balance within the WMB. This tends to increase the saline content of the deep water flowing through Gibraltar to the Atlantic [Kemp 2005] and could influence the Global Climate System through perturbations to the North Atlantic Oscillation (10-to-20-year delay). Figure 1 presents a hypothetical framework linking Western Mediterranean Basin (WMB)-specific atmospheric-oceanic processes, and their possible feedbacks, to effects at the hemispheric [Ulbrich *et al.* 2003] and global scales [Hamelin 1989; Savoie *et al.* 1992; 2002; Prospero and Lamb 2003, Kemp-Shellnhuber 2005; Gangoiti *et al*. 2006].

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Boreal Forests and Climate Change: Changes in N cycling and N_2O Emissions?

A contribution to ACCENT CCAQ: Group 2

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Summary

Boreal forest ecosystems are currently nitrogen (N) limited. As a result, the N cycling is closed, and practically all the N in the system remains there. Losses of N in the form of N_2O emissions are very small. We used the forest growth model (MikroForest) to assess the effects of increased temperature on N losses in a boreal forest within a 100 years period. An increase in soil temperature enhanced soil organic matter (SOM) decomposition and led to an increase in the release of ammonium (NH_4^+). We assumed that the increased availability of mineral N acts in a similar way as N fertilization. From a regression of N_2O emissions against N fertilization, we calculated the future emissions of N_2O from boreal forest soil. In our calculations the N_2O emissions from boreal forests do not significantly increase due to temperature increase. However, the uncertainties in these estimates of the future N_2O emissions from boreal forest region remain very large and call for further research.

Introduction

In present climate most of the boreal forests have a closed nitrogen cycle, which means that the nitrogen coming into the forest is retained there, and cycled internally. Losses of N in the form of N_2O emissions are very small [Schiller and Hastie, 1996; Brumme *et al.*, 2005; Maljanen *et al.*, 2006; Pihlatie *et al.*, 2007]. Climate change and the expected temperature increase may change C and N cycling in boreal forest soil, and affect the production of trace gases such as N_2O and NO. It is hypothesised that the temperature increase will enhance soil organic matter (SOM) decomposition and consequently increase the availability of ammonium (NH_4^+) in the soil. A further question is whether the increased availability of mineral N in the soil has a similar effect on N cycling as forest N fertilization. In general, N fertilization increases soil emissions of N_2O and NO [*e.g.* Brumme and Beese, 1992; Sitaula *et al.*, 1995; Butterbach-Bahl *et al.*, 1998; Rennenberg *et al.*, 1998; Venterea *et al.*, 2003; Ambus and Robertson, 2006]. However, experiments with forest N fertilization have shown that forest ecosystems with different fertility status respond differently to the additional N input.

Fluxes of N in boreal forest in current climate

We studied N pools and fluxes in a Scots pine dominated boreal forest during 1996 to 2006. The measurements were conducted at Smear II –station in Hyytiälä, southern Finland (61° 51’ N, 24° 17’ E). During this 10 year period the concentrations of dissolved organic nitrogen (DON), nitrate (NO_3^-) and ammonium (NH_4^+) in the incoming rainfall, through-fall and stem-flow, and N pools in litter-fall, and in the soil were measured. Losses of N were measured as N_2O and NO emissions, and as leaching of DON, NO_3^- and NH_4^+ from the outlet of the catchment area.

The plant available mineral N pool (0.32 g N m^{-2}) in the soil was 1-2 orders of magnitude smaller than the pool of dissolved organic nitrogen (DON) (2.9 g N m^{-2}), but both of these were only small fractions of the total N pool of the soil (145 g N m^{-2}). Atmospheric N deposition, as the sum of dry and wet deposition (0.5 g N m^{-2} yr^{-1}), was the only external input into the forest ecosystem. Most of the deposited N remained in the forest canopy and only small amounts were detected in the through-all and stem-flow waters. Litter-fall was the most important and the largest annual input of N into the soil system (6 g N m^{-2} yr^{-1}). Losses of N into the atmosphere in the form of N_2O and NO, and into water ways as NO_3^- or DON were negligible. Periodically the forest soil acted as a sink for N_2O, however, overall the site was a small source of N_2O [Pihlatie *et al.*, 2007]. During periods of high rainfall, small amount of DON was leached from the forest soil. The annual emissions of N_2O and leaching losses of DON each were 0.03 g N m^{-2} yr^{-1}.

Fluxes of N in boreal forest in changing climate

Changes in the N cycling during a 100-year forest growth period were investigated by means of a forest growth model MikroForest described by Hari and Kulmala [2008]. This model couples carbon and nitrogen cycling, and it predicts the development of forest vegetation at one year time steps. Proteins in soil organic matter decompose in enzymatic processes into amino acids and eventually NH_4^+ is released.

In a current climate the modelled release of NH_4^+ into the soil remained relatively stable during the forest growth period of 100 years (see Figure 1a). In a scenario of temperature increase by 3 °C during 100 years, the modelled release of mineral N into the soil at the end of the period was 1.5 times higher than that in the current climate (Figure 1b). This resulted from accelerated enzymatic decomposition reactions in the soil.

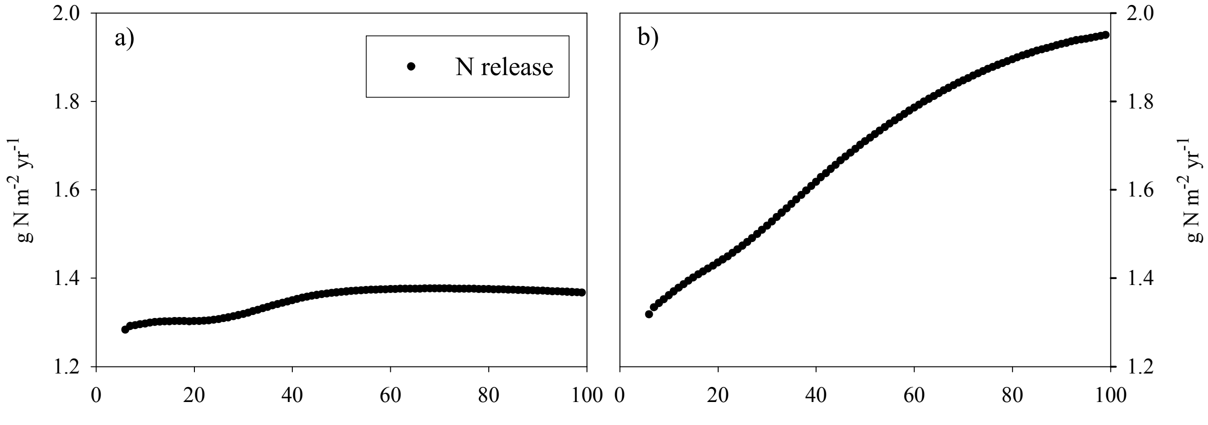

Figure 1. Modelled release of mineral nitrogen into boreal forest soil during a 100 years forest growth period, a) in present climate with no increase in temperature, and b) in future climate with a 3 °C increasing linear trend in temperature.

As mentioned above, the data on N_2O emission rates from coniferous forest ecosystems with different N deposition or N fertilization rates is limited. Also, there are very little studies available on the effects of increasing temperature on N turnover in boreal region. If we assume that the effect of increased release of NH_4^+ in boreal forest soil is similar to that caused by anthropogenic nitrogen deposition onto forest ecosystems, we can roughly estimate the changes in N_2O emissions. From a regression of observed N_2O emission against nitrogen deposition in N fertilized forest ecosystems in temperate and boreal zone (Figure 2) we get an estimate of N_2O emission at a certain N deposition rate. The current N_2O emission from boreal forest soils is approximately 0.03 g N m^{-2} yr^{-1} [Maljanen *et al.*, 2006; Pihlatie *et al.,* 2007]. Assuming that the annual release of NH_4^+ into coniferous forest soil increases by approximately 1.5 times the current release (see Figure 1), the corresponding N_2O emission in 2100 would be 1.14 times the current emission. This implies that the N_2O emissions in the year 2100 would not significantly differ from the current emissions.

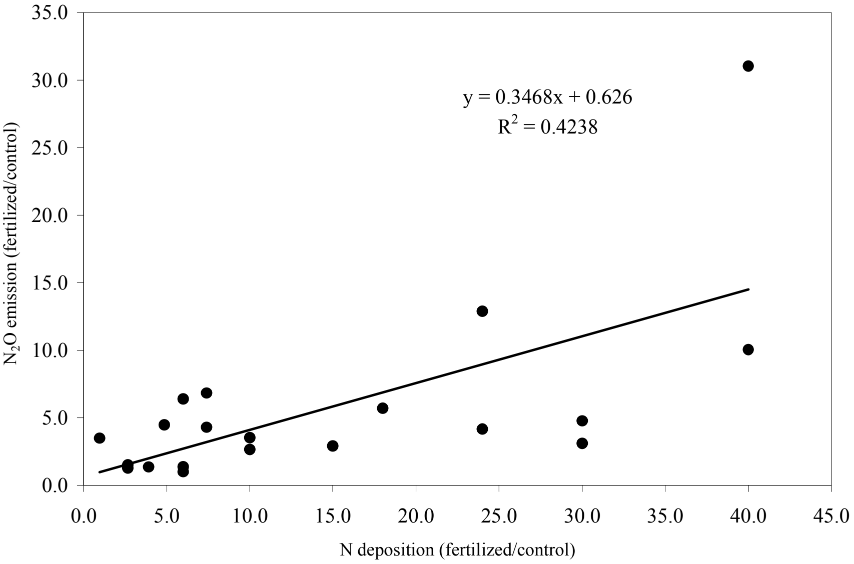

Figure 2. Nitrous oxide (N_2O) emission against N deposition from forest fertilization experiments in boreal and temperate forest ecosystems. Both the N_2O emission (y-axis) and the N deposition (x-axis) are expressed as emission or deposition factors that are the emissions or deposition from fertilized plots divided by the emission or deposition from control plots. Data from Bowden *et al.* [1991], Brumme and Beese [1992], Matson *et al.* [1992], Sitaula *et al.* [1995], Klemedtsson *et al.* [1997], Papen *et al.* [2001], Ambus and Robertson [2006].

Upscaling and uncertainties

The area of boreal forest is 16.6 × 10^{12} m^{-2}, thus the magnitude of N_2O emission from boreal forests in the present situation is approximately 0.5 Tg N yr^{-1}. In the year 2100 after a temperature increase by 3 °C and an accelerated release of mineral N into the soil, the emissions would be 0.6 Tg N yr^{-1}. These calculations indicate that the N_2O emissions from boreal forest region do not seem to increase markedly within next 100 years. However, it is clear that the uncertainties related to the calculation of this estimate are very large. The upscaling from current emissions to future do not take into account, for instance, possible changes in tree species composition or effect of soil moisture on N_2O forming processes. In conclusion, there is an urgent need to better understand the effects of slow and long-term additions of N on soil processes and trace gas emissions in boreal forest soils.

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Influence of Climate on NO and N_2O Emission – Lessons from the NOFRETETE Project

A contribution to ACCENT CCAG: Group 2

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Summary

Soil emissions of NO and N_2O were measured continuously at high frequency for more than one year at 15 European forest sites as part of the EU-funded project NOFRETETE. The locations represent different forest types (coniferous/deciduous) and different nitrogen loads. Geographically they range from Finland in the north to Italy in the south and from Hungary in the east to Scotland in the west.

The highest NO emissions were observed from coniferous forests, whereas the lowest NO emissions were observed from deciduous forests. The NO emissions from coniferous forests were highly correlated with N-deposition. The site with the highest average annual emission (82 g NO-N m^{-2} h^{-1}) was a spruce forest in South-Germany (Höglwald) receiving an annual N-deposition of 2.9 g m^{-2}. NO emissions close to the detection limit were observed from a pine forest in Finland where the N-deposition was 0.2 g N m^{-2} y^{-1}. The correlation between N_2O emission and N-deposition was weaker than for NO. The highest average annual N_2O emission (20 g N_2O-N m^{-2} h^{-1}) was found in an oak forest in the Mátra mountains (Hungary) receiving an annual N-deposition of 1.6 g m^{-2}.

It has been demonstrated in numerous studies that the temporal variation of nitrogen oxides emission within a specific site is clearly related to soil moisture and soil temperature. When comparing annual emissions on a regional scale, however, factors such as nitrogen deposition and forest and soil type become much more important.

Within a location increasing temperature will cause increasing emission. Changing soil moisture can result in both an increase and a decrease depending on whether it is NO or N_2O and where the optimum soil moisture for NO emission is. The overall most important driver for the emission is the N input.

Introduction

NO and N_2O emissions are known to vary considerably with both soil temperature and soil moisture and are therefore strong functions of climate [Smith *et al.*, 1998]. However, the relationships are not simple and not the same for NO and N_2O. It is therefore important to study these relationships over a range of climates at long time-scales to cover different seasons for each locality.

NO and N_2O emissions were measured continuously at 15 different forest sites as part of the EU-funded project NOFRETETE [Pilegaard *et al.*, 2006]. The measurements were made by chamber methods, either by manual measurements or by fully automated systems at a high frequency (up to hourly) throughout at least an entire year. Emission measurements were carried out using either the dynamic (NO) or the static chamber (N_2O) technique. The locations chosen included different types of forests (coniferous and deciduous) in different European climates, ranging from boreal to temperate continental forests and from Atlantic to Mediterranean forests. Furthermore the sites differ in atmospheric N-deposition ranging from low deposition (0.2 g N m^{-2} a^{-1}) to high deposition (4 g N m^{-2} a^{-1}).

This report focuses on the influence of the climate-related parameters, temperature and soil moisture, on the NO and N_2O emission.

Results

The relationships of the emissions of NO and N_2O, with the parameters nitrogen deposition, forest type, age, C/N, pH, soil temperature and water-filled pore space (WFPS) were investigated by means of stepwise multiple regression analysis.

NO emission was dependent on forest type and positively correlated with nitrogen deposition. The parameter WFPS was tested for curvature by including a quadratic term, but this was not significant. Separately performed regression analyses for deciduous and coniferous forests showed, however, that the relationship between nitrogen deposition and NO emission was only significant for the coniferous forests:

$$(\text{NO } (\mu\text{g N m}^{-2}\text{ h}^{-1}) = -13.9 + 25.5 \text{ [N deposition } (\text{g m}^{-2}\text{ a}^{-1})], r^2=0.82)$$

The N_2O emission was significantly negatively correlated with both the C/N ratio and the age of the stands; a logarithmic transformation of N_2O emission improved the significance of the correlation, see Figure 1.

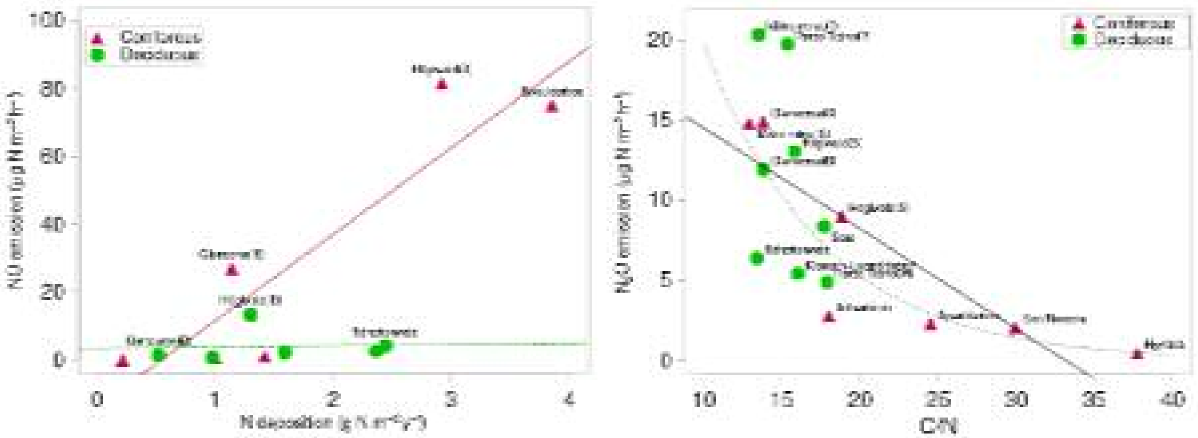

Figure 1. Left: NO emission (µg N m^{-2} h^{-1}) as a function of nitrogen deposition (g N m^{-2} a^{-1}). Regression lines (solid = significant, dashed = non significant) for coniferous and deciduous sites, respectively. Right: N_2O emission (µg N m^{-2} h^{-1}) as a function of C/N ratio. The full line represents a linear regression and the dotted line a logarithmic regression.

Influence of temperature and soil moisture

Production of NO and N_2O in soils is primarily driven by microbial processes such as nitrification and denitrification [Firestone and Davidson, 1989], therefore soil temperature is a key variable affecting the emission rates of both gases. Emissions of both NO [Slemr and Seiler, 1984] and N_2O [Skiba *et al.*, 1998] increase with increasing soil temperature due to the fact that rates of enzymatic processes generally increase with temperature as long as other factors (*e.g.* substrate or moisture) are not limiting. Soil water acts as a transport medium for NO_3^- and NH_4^+ and influences the rate of O_2 supply and thereby controls whether aerobic processes such as nitrification or anaerobic processes such as denitrification dominate within the soil.

While N_2O emissions are known to increase at higher water contents through larger losses from denitrification [Papen and Butterbach-Bahl, 1999] the relationship between the NO flux and the soil water is more complex. Due to limited substrate diffusion at very low water content and limited gas diffusion at high water content, nitric oxide emissions are suspected to have a maximum at low to medium soil water content, see Figure 2.

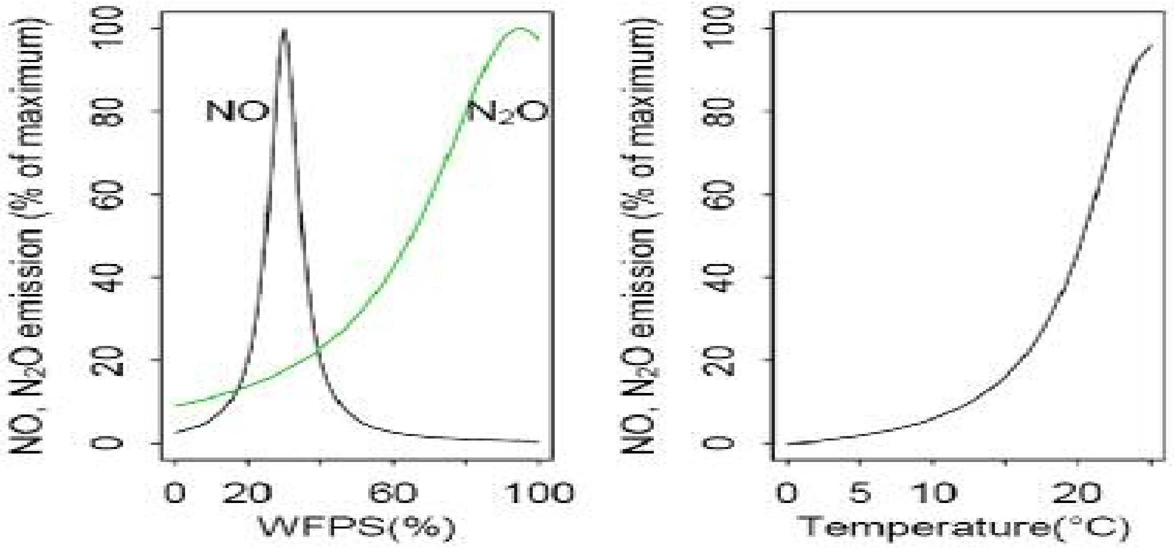

Figure 2. Generalized relationships of NO and N_2O emission with water filled pore space (WFPS) and temperature.

The effects of soil moisture and temperature on NO and N_2O emission were studied in a laboratory experiment with soil cores from some of the same field sites as in the present study (Parco Ticino(M), Schottenwald, Klausen-Leopoldsdorf, Achenkirch, Höglwald (spruce) and Hyytiälä) [Schindlbacher *et al.*, 2004] . Soil moisture and temperature explained most of the variations in NO (up to 74 %) and N_2O (up to 86 %) emissions for individual soils. NO and N_2O were emitted from all soils except from the boreal pine forest soil in Finland, where the laboratory experiment showed that NO was consumed. NO emissions from the German spruce forest ranged from 1.3 to 608.9 μg NO-N m^{-2} h^{-1} and largely exceeded emissions from other soils. Average N_2O emissions from this soil tended also to be highest (171.7 ± 42.2 μg N_2O-N m^{-2} h^{-1}), but did not differ significantly from other soils. NO and N_2O emissions showed a positive exponential relationship to soil temperature.

The results from the annual averages of field data did not show any significant relationship to soil temperature for neither for NO nor for N_2O emission. Schindlbacher *et al.* [2004] also showed that N_2O emissions increased with increasing WFPS or decreasing water tension, respectively. Maximum N_2O emissions were measured between 80 and 95 % WFPS or 0 kPa water tension. The optimal moisture for NO emission differed significantly between the soils, and ranged between 15 % WFPS in sandy Italian floodplain soil and 65 % in loamy Austrian beech forest soils (Figure 3). For the field data WFPS was not a significant parameter for N_2O emission, but had a positive significant effect on NO emission. The annual average WFPS in the field was higher than the optima found for NO in the laboratory experiment, but since not all field sites were studied in the laboratory it is difficult to provide a general conclusion.

The interannual variation within single sites clearly showed relationships to both temperature and soil moisture. An important factor for N_2O emission is freeze-thaw events which can produce a significant outburst of N_2O [Kitzler *et al.*, 2006].

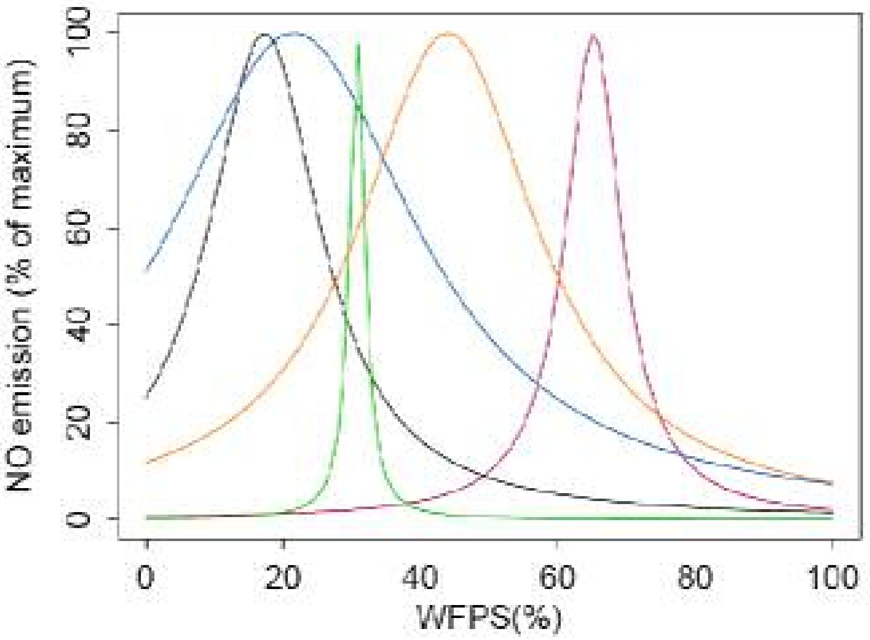

Figure 3. The relationship of NO emission and water filled pore space at different localities in the NOFRETE project.

In general, rather clear relationships between nitrogen oxides emission and soil moisture and soil temperature can be found within a single locality when studying short-term variations. However, using the same parameters when comparing annual values from different localities within a large region as in this study does not necessarily reveal comparable relationships since other factors such as soil properties, stand age, and site hydrological conditions interfere. Equally, in a study of 18 European forests Janssens *et al.* [2001] found large differences in observed annual soil respiration and total ecosystem respiration, but despite good correlations with temperature within the single forests, the differences between the forests were not correlated with mean annual temperature. They hypothesised that differences in soil respiration among forests are likely to depend more on forest productivity rather than on temperature.

Conclusions

The main driver for NO and N_2O emission is the N input. NO emission is directly related to N deposition, whereas N_2O emission is indirectly related via the C/N ratio. Temperature is an important variable for a specific site with increasing emissions of both NO and N_2O with increasing temperature. Soil moisture is another important variable. N_2O emission will increase with increasing soil moisture. In contrast, the relationship between soil moisture and NO emission shows an optimum moisture level where the emission is highest. The absolute value of the optimum differs from site to site and the effect of increasing soil moisture may therefore be a decrease or an increase in NO emission depending on where the actual soil moisture is in relation to the optimum.

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Polar Boundary Layer Ozone Depletions: A Link to Climate Change and Air Pollution

A contribution to ACCENT CCAQ: Group 2

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Introduction

Each year in spring, periods of partial or complete ozone removal from the boundary layer are observed in stations in the Arctic and Antarctic. These so called ozone depletion events (ODE) have been linked to catalytic ozone destruction by halogens, in particular bromine. One key player, bromine oxide (BrO) has been observed from the ground and from space [Wagner *et al.*, 1998 and 2001, Richter *et al.*, 1998 and 2002] and judging from the satellite maps, ozone depletion affects a large part of the sea ice covered areas in both hemispheres each spring. More recently, another halogen oxide (IO) could also be detected from space [Schönhardt *et al.,* 2007], but it is not yet clear what its role in ozone depletion is.

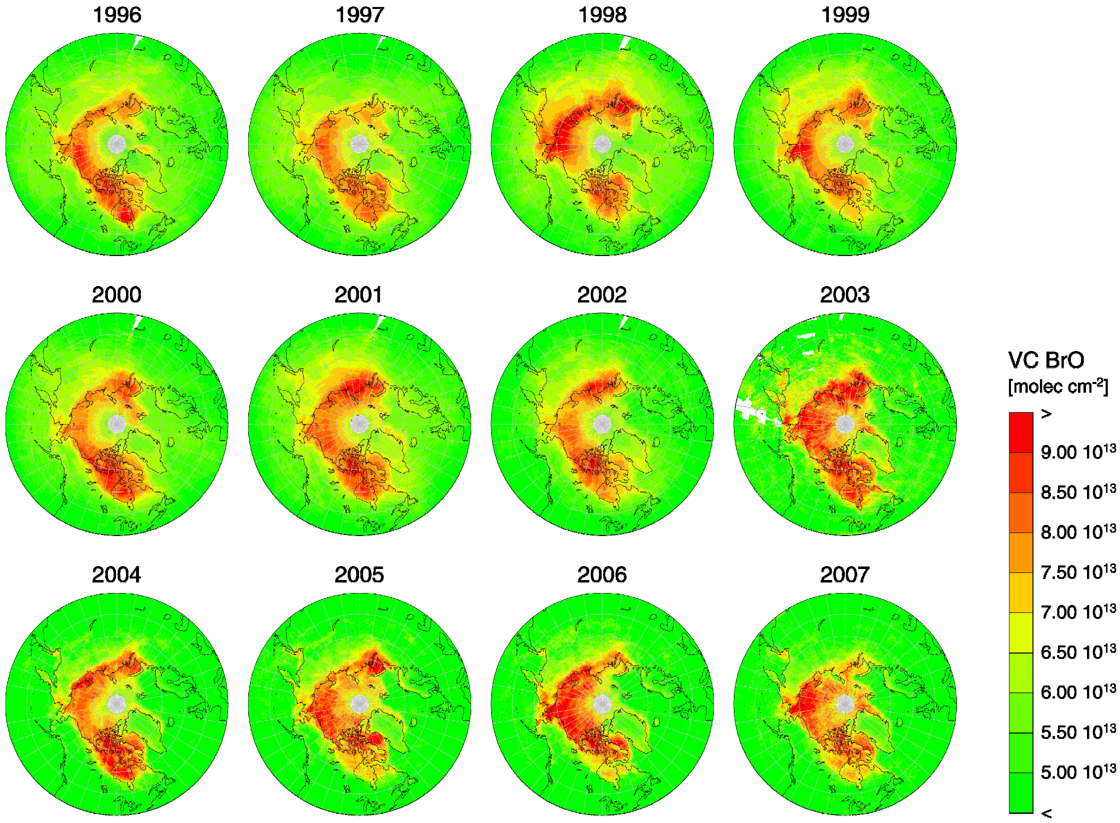

Figure 1. BrO total columns for April from 1996 – 2002 (GOME measurements) and 2003 – 2007 (SCIAMACHY). While the overall pattern is similar between the years, the details and also the absolute values can vary significantly. Daily BrO maps from SCIAMACHY are available at: http://www.iup.uni-bremen.de/doas/scia_data_browser.htm?gas=bro.

The source of the bromine is sea salt which is released to the gas phase through heterogeneous reactions on ice or snow surfaces or aerosols. While the chemistry of the ozone depletion is well understood, and recycling of bromine in aerosols can be modelled, the exact mechanism of initial release is still under discussion. A detailed overview on polar ozone depletion and the link to halogens can be found in the review of Simpson *et al.* [2007].

Bromine is also released to the atmosphere through other mechanisms, *e.g.* volcanic eruptions [Bobrowski *et al.,* 2003, *Afe et al.*, 2004] and measurements have shown the presence of a global background of tropospheric BrO of unknown origin [Richter *et al.,* 2002, Van Roozendael *et al.*, 2002, Fietkau *et al.*, 2007, Theys *et al.*, 2007].

Here, we concentrate on BrO released in the polar boundary layer in spring and possible impacts of climate change on BrO levels and their link to pollution.

Open questions

The morphology, mechanisms, and impacts of polar ozone depletion events and the halogen chemistry involved have been studied for several decades. Many parts of this system are well understood [Simpson *et al.*, 2007 for an overview] but several open questions remain, in particular with respect to the effect of climate change.

1) What are the conditions needed for polar boundary layer BrO explosions?

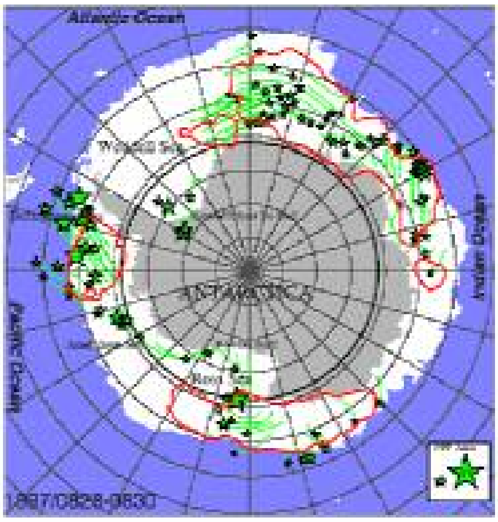

Figure 2. Sea ice coverage (in white), BrO distribution (red isoline), areas of potential frost flowers (stars) and 1 day forward trajectories from these locations for three days in August 1997. Areas with the potential for frost flower formation agree well with areas where enhanced BrO is observed from satellite. The agreement improves further if one day of transport is allowed for. Within the black circle, light intensities are too low for efficient photochemistry and thus no BrO is formed in spite of the potential for frost flowers.

Observations show, that BrO explosions are linked to low temperatures and contact of air masses with specific surfaces, either first year sea ice [Wagner *et al,* 2001] or areas with the potential for frost flower formation [Kaleschke *et al.*, 2004]. In addition, sun light is necessary to support the rapid photochemistry involved.

So far, no direct observational support could be found for any of the suggested release mechanisms of bromine. Most evidence comes from correlation of low ozone or high BrO measurements with air mass origin, surface contact, and ice and temperature observations. Attempts to measure BrO formation locally and link it directly to release mechanisms have not been successful so far. Although the pattern of BrO enhancements observed from space is similar between years, and autocatalytic release of BrO is reproduced in models once a certain level of BrO is reached, it is not clear how these BrO events are seeded.

For the assessment of a potential link between climate change and BrO events, knowledge of the exact mechanisms is needed. Without this information, one has to rely on investigation of those parameters which have a correlation with BrO events: fresh ice, low temperatures and sun light.

2) How is polar* BrO *going to react to changes in sea ice cover?

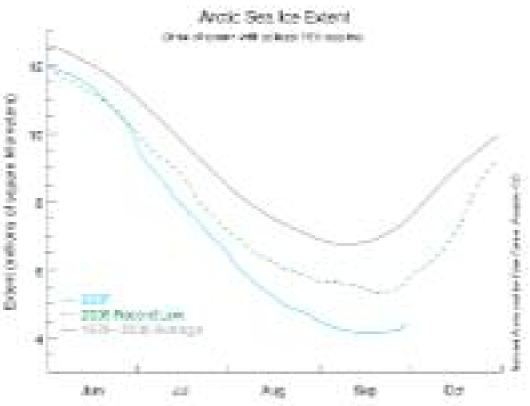

Figure 3. Sea ice coverage in the Northern Hemisphere for the average from 1979 to 2000 (grey line) and the recent values for 2007 (blue line). As can be seen, the overall sea ice coverage has nearly halved in summer but is only slightly reduced in spring. Figure from: http://nsidc.org/news/press/2007_seaiceminimum/20071001_pressrelease.html.

Measurements of sea ice in the Northern hemisphere indicate a rapid decrease in the area covered by sea ice in summer. This reduction in sea ice extent has been faster than predicted by models and is accompanied by a fast reduction in ice thickness. Lower sea ice cover has many consequences for the Arctic ecosystem, for climate (including the albedo feedback mechanism) and also for human activities which could be much more important in the future if the Arctic sea becomes shippable over extended time periods. Recent data on ice coverage can be found at http://nsidc.org/index.html.

The effect of changes in sea ice extent on Arctic BrO events is less clear. On the one hand, a reduction in sea ice extend reduces the area available for heterogeneous BrO release. However, it appears that BrO is mainly released from fresh ice or frost flowers forming on recently frozen leads in the ice, and a reduction in multi year ice will lead to an increase in first year ice in spring. From this argument, an increase in BrO events is to be expected. Changes in temperature also will play a role. BrO explosions have been observed to be linked to low temperatures, and as climate warms, these may be less frequent in the Arctic. As a result, one might expect a shift of the regions typically affected by BrO explosions, both in latitude and season.

A more indirect effect of climate change on BrO events may be through increased input of pollutants into the Arctic boundary layer. It is expected that emissions from shipping and mining in the Arctic will increase as ice retreats, and they will influence the chemistry on snow and ice as they deposit over summer [Law *et al.,* 2007]. In particular the pH is known to play a role in BrO release, and this is bound to change at least locally in the vicinity of shipping lanes.

The existing long-term data set of BrO measurements from space could be used to investigate whether or not BrO events have become more frequent in recent years. In a study on GOME data, Hollwedel *et al.* [2004] found tentative evidence for such an increase in BrO. However, the agreement between GOME and SCIAMACHY BrO measurements is not yet good enough to extend this study to the SCIAMACHY data record and it is therefore not yet clear, if this upward trend continues.

In summary, while it is to be expected that polar BrO explosions, in particular in the Northern Hemisphere will be impacted by climate change in many ways, it is not clear in which way. The most probable scenario is an increase in the frequency and spatial extent of BrO explosions over the next years.

3) What is the link between boundary layer* BrO *explosions and pollution?

Polar boundary layer BrO explosions can potentially impact on pollution in two different ways: directly, by reaction of bromine compounds with pollutants or other trace species in the atmosphere and indirectly by changing ozone levels.

A well known example of direct interaction of polar bromine chemistry with pollution is the link to mercury. Anthropogenic emissions of mercury have lead to a global background of gaseous mercury which is also present in the polar regions. It has been observed, that during ozone depletion events, gaseous mercury is also depleted while at the same time particulate mercury is enhanced. It is thought that reaction with BrO or HOBr can oxidize Hg(0) to Hg(I) or Hg(II) which can then deposit on snow and ice. If mercury is not re-emitted to the atmosphere (which at least partially it is), it will enter the oceanic food chain with snow melt in summer. It appears that this is one of the most important pathways of mercury input into the Arctic ecosystem and can explain at least part of the observed high mercury levels in Arctic population relying on local foods. An extensive review of mercury chemistry in Polar Regions and its link to halogen chemistry can be found in Steffen *et al.* [2007].

An indirect link between polar halogen chemistry and pollution is via ozone levels in the free troposphere. Ozone depletion events in polar spring affect large areas each year and constitute a net sink of ozone in the troposphere. The overall importance is unknown but expected to be small as the air volume from which ozone is removed is small due to the low boundary layer height in Polar Regions. Still, the ozone removed at the surface is replaced by ozone from the free troposphere and increasing intensity of BrO explosions in the Arctic and Antarctic could have an effect on mid-latitudes.

BrO from the polar regions is also transported to mid-latitudes, mainly to the Hudson Bay but occasionally also to other areas. Even though meteorological conditions in these regions will usually not support further bromine explosions, some ozone reduction will result from this halogen input. In fact part of the global BrO background observed from satellite and from the ground might originate from the polar boundary layer. Any change in polar halogen chemistry could therefore have an effect on the oxidizing capacity of the free troposphere.

As anthropogenic activities in the Arctic and possibly also the Antarctic intensify, pollution levels will increase and yet unknown interactions between halogens and pollutants could result, similarly to the known effects on mercury chemistry.

In summary, the main known link of polar halogen chemistry and pollution is via mercury deposition. There is also an effect on ozone levels but this is expected to be small. For the future, other interactions might become relevant as pollution levels in the Arctic increase.

Research needs

Research needs can be directly deduced from the open questions discussed above:

- the mechanism of Br release should be identified *e.g.* by statistical analysis of satellite data, ground-based in-situ measurements of halogen release and lab experiments on potential sources such as frost flowers
- the existing time series of satellite data needs to be homogenized to facilitate study of the trend over the last decade
- potential reaction pathways between halogen compounds such as BrO and HOBr and pollutants emitted by ships and mining should be investigated

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Biogenic VOC Emissions in Europe in the Light of a Changing Environment

A contribution to ACCENT CCAQ: Group 2

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Summary

Biogenic VOC emissions contribute significantly to reactive trace compound distribution to the boundary layer impacting radical as well as particle distributions with consequences for e.g. air quality and the earth surface energy balance. VOC emissions from natural sources are mainly depending on the emission active surface (land cover), temperature and light intensity being therefore very sensitive to anthropogenic changes on the environment. For a recent biogenic non methane VOC emission estimate for an extended European area and the years 1997, 2000, 2001 and 2003 a new database of input parameters was compiled. The semi-empirical BVOC emission model (seBVOC) uses these data considering in addition seasonality and forest canopy effects. In all years, highest BVOC emissions were observed in June, July and August with isoprene, monoterpenes and oxyVOC being emitted in almost equal amounts with a small contribution of sesquiterpenes (1 to 2 %). Highest BVOC flux densities were reported for Mediterranean countries and Portugal. BVOC emission is dominated by forest sources with about one third coming from other land use. The inter-annual variability is about ± 10 % considering cold as well as hot years serving as an example for a potential climate effect on BVOC emissions in the years around 2050. Non methane BVOC emissions may contribute to surface ozone levels up to 15 ppb for specific hot weather situations in southern Europe as well as to secondary particle formation.

Introduction

Biogenic Volatile organic compounds (BVOC) excluding methane are emitted mainly from vegetation being in general temperature and light dependent. Other biogenic VOC sources (animals and humans) are much smaller. The dominating biogenic compound emitted is isoprene [Simpson *et al.*, 1999]. In contrast to anthropogenic VOC (AVOC), BVOC are more reactive in the atmosphere with a pronounced emission maximum in the summer. During high pressure weather systems *e.g.* in June, July and August with low wind speed, high solar insulation and air humidity, combined with high NO_x levels and limited horizontal exchange, surface ozone is exceeding air quality standards in most cases (*e.g.* WHO 100 µg /m^3; 8 hour average). For example in 2003 and again in 2006 about more than 50 % of European urban population was exposed to air pollutant concentrations over certain limit values [EEA, 2007] despite precursor emission reduction legislation in place (*e.g.* VOC, NO_x EU NEC directive; UNECE CLRTAP Gothenburg protocol). In particular, NO_x emissions and surface ozone require further significant attention to meet the target limit values. With ongoing European emission reductions in anthropogenic precursor emission of air pollutants it becomes increasingly important to quantify correctly biogenic precursors for establishing effective local and regional air quality control measures to meet health and vegetation exposure limits. In this respect, VOC totals are not very helpful as ozone creation potential in the atmosphere is compound specific. Therefore, much more efforts have to be put into reducing uncertainties and knowledge gaps related to chemical compound specific source strength from the different emission categories both biogenic and anthropogenic, the effect of land use change, elevated temperature, longer sun shine periods, extended draught periods, increased storm activity. Recently, a potential negative feedback of increasing CO_2 in the atmosphere on isoprene emission from plants has been reported [Sharkey *et al.*, 2007]. On the other hand, ozone stressed vegetation seems to produce much more VOC compared to unstressed one [Schnitzler, IMK-IFU, personal communication]. But those effects deserve further investigation due to the limited number of plant as well as ecosystem responses studied. Here, results from a latest estimate on VOC emissions from forests and other land use of European and neighbouring countries are presented and discussed. Estimates of the year 2003 may serve as an example for BVOC emissions in a warmer future climate around the year 2050.

Scientific activities

Non methane BVOC emission estimates were calculated for the years 1997, 2000, 2001 and 2003 with a spatial resolution of 10 by 10 km and a temporal resolution of 1 hour using latest input information as part of quantifying natural emissions in Europe in the frame of the NatAir project [Friedrich, 2007; http://natair.ier.uni-stuttgart.de]. A new database was compiled containing land and forest distributions, foliar biomass densities, and leaf area index and plant as well as chemical compound specific emission potentials where available. The semi-empirical BVOC emission model [Smiatek and Steinbrecher, 2006] uses these data considering in addition seasonality of the emission potentials, light extinction within the canopy as well as leaf temperature, air humidity, wind speed, and solar angle as driving variables. Meteorological input fields were compiled with the MM5 model; ozone and particle near surface values were calculated using the CHIMERE model [Cruci *et al.*, 2007]. The new emission inventory considerable reduces the bias emerging from coarse land use information and lumped emission factors. The overall uncertainty of the BVOC estimates for western, southern, northern and central Europe is rated at a factor of two, being as high as a factor of four to 10 for eastern Europe, northern Africa, middle and south western Asia resulting from insufficient input data quality mainly on plant specific land use information and on lacking of plant species specific emission factors.

Scientific results and highlights

In contrast to anthropogenic VOC emissions with a more or less even source strength around the year, VOC emerging from biological sources peak in June, July and August (Figure 1). Taking the extraordinary warm year 2003 as an example for a possible future climate impact on BVOC emissions, biogenic sources will be about 10 to 15 % higher than the four years average from the years 1997, 2000, 2001, and 2003. This estimate does not include likely effects on BVOC source strength resulting from land use change, and feedback of increasing CO_2, photooxidants, draught periods and storm activity which may lower isoprenoid emission when considering the negative feedback of CO_2 or soil draught or increase VOC emission resulting from *e.g.* increased plant damage by increased storm activity and higher oxidant levels in a future atmosphere. In Europe isoprene and the totals of monoterpenes and oxyVOC are being emitted in almost equal amounts (Figure 2). The contribution of sesquiterpenes is small (1 to 2 %). Highest BVOC flux densities were reported for Mediterranean countries and Portugal. Compared to an older inventory of Simpson *et al.* [1999], the current estimate results in considerable higher BVOC emissions (*e.g.* Mediterranean countries) and in a changed biogenic VOC emission split (*e.g.* France, Germany) with less isoprene but more monoterpenes and oxyVOC being emitted. Ozone and particles formed from biogenic VOC precursors may amount to 15 ppb (Porto, Portugal) and 9 µg m^{-3} (western parts of Spain), respectively, in summer 2000 [Cruci, LISA, personal communication].

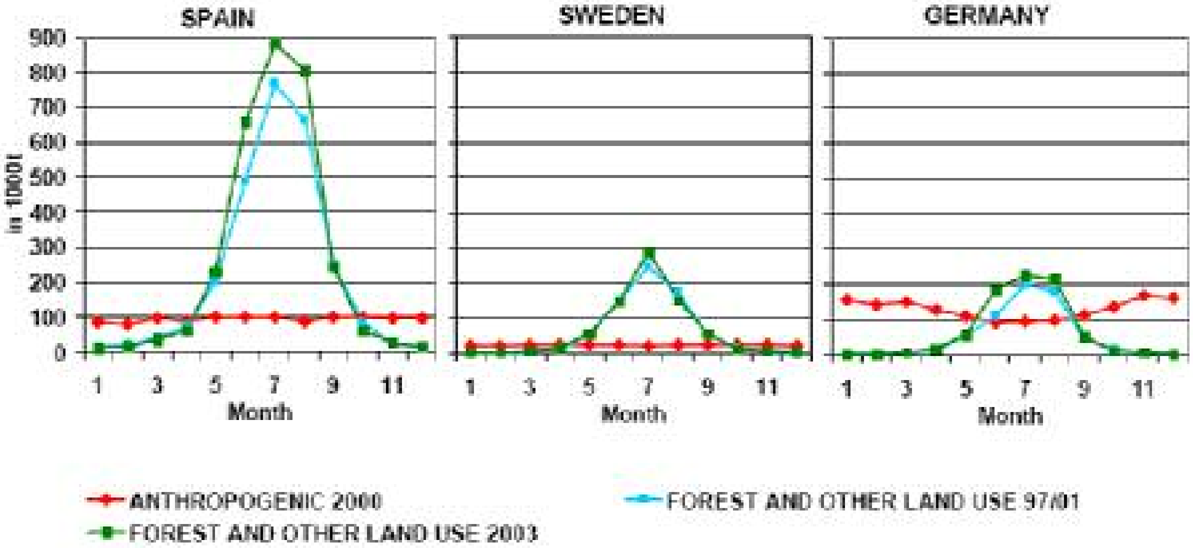

Figure 1. Monthly variability of AVOC and BVOC emissions for selected European countries and specific years [adopted from Friedrich, 2007].

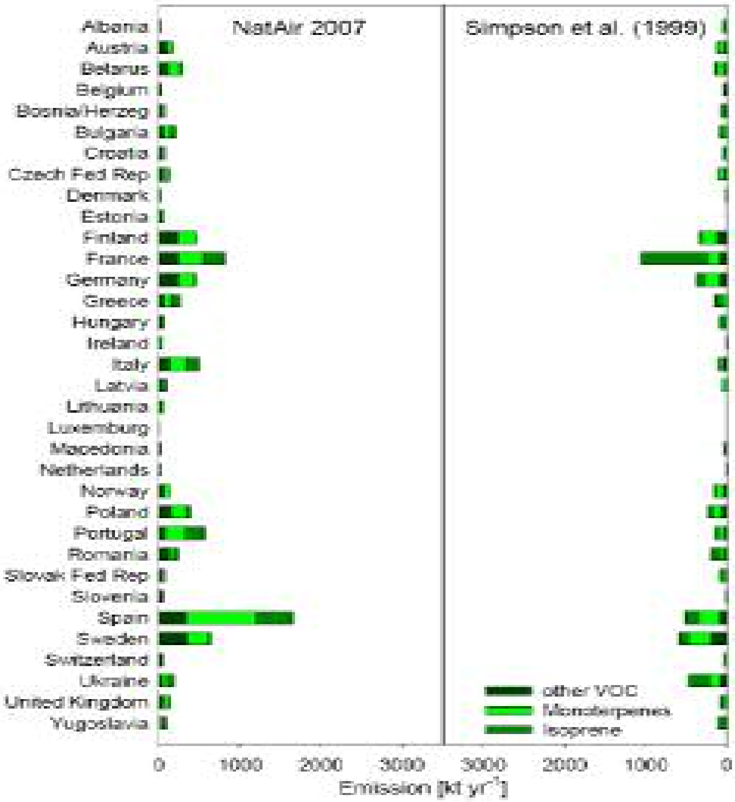

Figure 2. Annual forest VOC emission estimates for European countries. Both inventories report yearly averaged emissions. Other VOC reflect oxyVOC only [adopted from Steinbrecher *et al.*, 2007].

Future outlook

Great progress has been achieved in understanding the processes governing VOC emission from vegetation in the last years as well as in improving land cover classification. On the basis of this new information an updated BVOC emission estimate for an extended area of Europe (EU member states including countries from eastern Europe, central Asia, Middle East and North Africa) has been compiled. Uncertainties in this BVOC emission estimate are still greater as a factor of two as estimated based on a still too coarse land use classification in particular for non EU15 countries, a still large number of default emission factors, and unknown feed back effects of interacting emission controlling parameters (*e.g.* CO_2, soil draught, photooxidants). As BVOC are governing atmospheric chemistry and thus the cleansing capacity in late spring and summer in large parts of Europe, it is of great importance to reduce uncertainties in the estimates by studying the impact of major global change factors (CO_2, ozone, draught, storms) on the source strength and VOC split emitted by current as well as estimated future vegetation.

Further development of tree species distribution maps with high spatial resolution also for extended European areas.

For setting up effective air quality control measures it is further needed to:

* Intensify research on second order BVOC oxidation in the atmosphere for elucidating short-term and long-term effects on air quality (e.g. contribution to ozone peak and background levels) and climate,

* Develop coupled predictive meteorological-VOC emission- air chemistry-transport models for studying the impact of biogenic sources on air quality suitable for small scale and larger scale applications, and

* Validate and further improve these models by integrated field studies in key ecosystems of Europe including also economic plants (*e.g.* used in bio-fuel production)

In the future, when all directives for emission control of anthropogenic compounds are fully in place biogenic and natural emissions will become more and more important in air chemistry in the lower troposphere of Europe being also an important player in air pollution episodes in particular having in mind the increasing area of managed forests for building up CO_2 sinks and producing biomass for fuel production using fast growing tree species in particular the high VOC emitters *Eucalyptus, Popular* or palm trees.

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12 Contributions from Group 3 Participants

Investigating changes in aerosols, SOA, dust and their precursors with changing temperature, humidity and land use.

Impacts of Climate Change and Global Emissions on US Air Quality: Development of an Integrated Modelling Framework and Sensitivity Assessment

A contribution to ACCENT CCAQ: Group 3

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Summary

Future changes in climate and global pollutant emissions may provide additional challenges to air quality management in the US. This report summarizes the results of four years of research on the impacts of global change on $PM_{2.5}$ and ozone in the US.

Sensitivity scenarios and future climate/emissions scenarios are investigated using both regional and global modeling tools. Additionally, a comprehensive Global-Regional Climate Air Pollution Modelling System (GRE-CAPS) has been developed combining the GISS global climate and chemistry model, with regional meteorological (MM5) and multiscale chemical transport (CTM) model (PMCAMx). The modelling system describes atmospheric chemistry and dynamics from global to regional scales. A set of future scenarios that spans permutations of emissions and climate changes has been simulated by this modelling system to quantify their effects individually and together.

The ability of GRE-CAPS to predict present-day ozone and $PM_{2.5}$ levels has been evaluated and shown to be similar to that of PMCAMx [Dawson *et al.*, 2007c]. Sensitivity studies of ozone and $PM_{2.5}$ to changes in individual meteorological parameters have been performed [Dawson *et al.*, 2007a; Dawson *et al.*, 2007b] to assess and quantify where major sensitivities to climate/meteorology lie. The GISS GCM/CTM has been used to assess changes in background levels of ozone and $PM_{2.5}$ [Racherla and Adams, 2006] resulting from climate change alone. The GISS GCM/CTM has also been used to assess ozone and $PM_{2.5}$ changes in the US with longer simulations than feasible with GRE-CAPS and to separate the effects of interannual variability from climate change *per se* [Racherla and Adams, 2007a; Racherla and Adams, 2007c]. A suite of future climate and emissions scenarios has been developed to assess the relative impacts of climate change, domestic emissions, intercontinental transport, climate-sensitive emissions, and global methane on US air quality [Racherla and Adams, 2007b], and these scenarios have been simulated in the GRE-CAPS model [Dawson *et al.*, 2007d; Dawson *et al.*, 2007e].

Introduction

Reductions of high ozone and airborne particulate matter (PM) concentrations are major objectives of air quality management in the United States. Design of emission control strategies involves establishing the response of pollutant concentrations to changes in emissions assuming that meteorology and background pollution levels remain constant. Even with these simplifying assumptions, the task is challenging because of the complexity of ozone photochemistry, the chemical complexity of atmospheric PM, the existence of thousands of airborne organics, the complex interplay between atmospheric chemistry and atmospheric dynamics, the difficulty in quantifying natural contributions, or understanding the role of the long-range transport of pollution.

Every stage in the life cycle of an atmospheric pollutant depends on weather and climate. Biogenic emissions of isoprene and terpenes, precursors of ozone and secondary organic aerosol (SOA), depend on sunlight and temperature including longer-term temperature variations [Petron *et al.*, 2001]. Gasoline volatilization, a significant source of VOCs in the urban atmosphere, is temperature-dependent. Ammonia emissions increase significantly with temperature [Pinder *et al.*, 2004a; Pinder *et al.*, 2004b]. Gas-phase reaction rates are sensitive to temperature [Sillman and Samson, 1995] and influence the rates of ozone formation and VOC oxidation to semi-volatile species that form SOA. Temperature is also a controlling factor for PM by driving the partitioning of nitrate, ammonia, and semi-volatile organics between the gas and particle phases. Ozone concentrations depend on cloudiness via the photolysis rates of NO_2 and other species. Cloud droplets influence air quality as sites for aqueous oxidation of sulfur dioxide to sulfate [Jacob, 1986], a principal component of PM. Boundary layer mixing is important in any urban air pollution episode as vertical mixing dilutes pollutants. Stronger winds move pollutants out of an urban area, albeit at the cost of lower air quality downwind. Finally, precipitation is an important removal mechanism for species such as PM, soluble organics, ammonia, and nitric acid. Changes in these meteorological parameters will necessarily impact concentrations of ozone and PM.

Global economic development also has implications for air quality in the United States. It has been recognized that intercontinental transport of pollutants contributes to air quality problems in the US. Recent modelling suggests that sources outside the United States contribute several ppbv to US ozone concentrations [Hudman *et al.*, 2004; Jacob *et al.*, 1999] with a similar result for Europe [Jonson *et al.*, 2001]. Anthropogenic aerosol from Asia also contributes to “background” PM in the United States [Park *et al.*, 2004]. Contributions from intercontinental transport are likely to increase as global economic development progresses.

These issues have been investigated using a multi-pronged approach. The PMCAMx regional CTM has been used to investigate the sensitivity of ozone and PM to individual meteorological parameters. The GISS GCM/CTM has been used to investigate global-scale changes in intercontinental transport, biogenic emissions, and background pollutant concentrations. Finally, the newly developed GRE-CAPS modelling system has been used to downscale the results of the global-scale future scenarios to regional and urban scales.

Scientific activities

Regional CTM simulations of sensitivity to climate parameters

A number of sensitivity simulations have been performed and analyzed to evaluate the impact of climate change on annual average $PM_{2.5}$ concentrations, MDA8 ozone concentrations, and ozone exceedances. Four ten-day periods have been modelled so that all four seasons can be examined: 12th to 21st July 2001, 1st to 10th October 2001, 6th to 15th January 2002, and 1st to 10th April 2002. The first three days from each period were used as model initialization days and are excluded from the analysis. For each season, a base case and a suite of sensitivity simulations are performed. Each sensitivity simulation tests a single meteorological variable by perturbing it a given amount. The perturbed variables include temperature, wind speed, absolute humidity, mixing height, cloud liquid water content (LWC) and optical depth (OD), cloudy area, precipitation rate, and precipitating area. Except for cloud, precipitation, and mixing height changes, all perturbations are imposed uniformly in space and time on the modelling domain. This activity is described in more detail in the published literature [Dawson *et al.*, 2007a; Dawson *et al.*, 2007b].

Results from global climate-chemistry simulations

A "unified" global model of climate, ozone photochemistry, and aerosols (the GISS GCM/CTM) was used to predict the effect of climate change on future ozone and PM levels globally. Emissions were held at constant (present) levels to isolate the effect of climate change. A future climate was imposed on the global model by changing the sea-surface temperatures and associated ocean boundary conditions, which resulted in a mean increase of 1.7 °C in global surface air temperatures, an increase in lower tropospheric specific humidity of 0.9 g H_2O per kg air, and a mean increase in precipitation of 0.15 mm d^{-1}. Impacts on annual-average $PM_{2.5}$, annual-average ozone, and ozone episodes were analyzed across the globe but with a focus on the eastern United States as well. More details can be found in several publications [Racherla and Adams, 2006; Racherla and Adams, 2007a; Racherla and Adams, 2007c].

Development of a coupled global to regional climate and air quality modelling system

A fully coupled global to regional scale model of climate change and air quality has been developed. In this Global-Regional Climate Air Pollution Modelling System (GRE-CAPS), present and future climates are simulated by the GISS-II' GCM, which is coupled to a gas-phase and aerosol chemistry model. Meteorology generated by the GCM is downscaled to the regional modelling domain using the MM5 regional climate model. The downscaled meteorology is passed on to the regional chemical transport model PMCAMx. In addition to the downscaled meteorology, the chemical boundary conditions for the regional model are derived from the cells in the global model that correspond to the boundaries of the regional domain, simulating transport into the domain.

The GRE-CAPS modelling system is evaluated for the present day, with comparisons between model-predicted and measured ozone and speciated $PM_{2.5}$ concentrations. The model was used to simulate five present-day Januaries and six present-day Julys. The biases and errors in GRE-CAPS-predicted ozone concentrations were similar to those of PMCAMx when used for standard retrospective modelling. The fractional biases in mean daily peak ozone concentration and mean daily maximum 8-hour average ozone concentration are both less than 10 %. The model-predicted distribution of peak hourly and daily maximum 8-hour average values agreed rather well with the measured distribution. The predictions of $PM_{2.5}$ concentrations by GRE-CAPS were also of similar quality to those of PMCAMx driven by historical meteorology. The fractional biases in the predictions of total $PM_{2.5}$, sulfate, ammonium, and nitrate were all less than 25 % in both January and July. The model agrees well with organic $PM_{2.5}$ measurements from the IMPROVE network, though there is less agreement with measurements from the STN network. The GRE-CAPS system is shown to adequately reproduce ozone and $PM_{2.5}$ concentrations for the present day, with model performance similar to that of PMCAMx for standard retrospective episode modelling.

Assessment of global change impact on future air quality

A total of 9 model simulations were performed with GRE-CAPS (see Table 1). The "Run duration" column in Table 1 refers to the length of time simulated by the global model component only; shorter time periods are down-scaled with PMCAMx. These simulations have been designed to explore the relative effects of the changes in future climate, U.S. and global anthropogenic emissions (increase/decrease), climate-sensitive emissions, CH_4 abundance, and long-range transport on air pollution over the United States. So as to be useful to near-term air quality policy, we consider global change scenarios corresponding to the 2050s. As the projected 2050s climate change for most IPCC SRES scenarios is nearly the same [Intergovernmental Panel on Climate Change (IPCC), 2001], we use the A2 2050s climate as a representative future climate. However, the scenarios diverge significantly with regards to their projected regional distributions of emissions, which will impact U.S. O_3 and $PM_{2.5}$ concentrations differently. Therefore, to examine the sensitivity of U.S. $O_3/PM_{2.5}$ to regional emissions increases (decreases), the A2 and B1 scenarios, which have overall higher and lower emissions for the United States, respectively, have been chosen.

Table 1. Summary of the runs performed. The first 6 months for runs 1-8 are considered as model initialization; run 9 utilizes 2 months of initialization time per summer. Climate-sensitive biogenic emissions are allowed to vary with the simulated climate in all runs except 9; please see Racherla and Adams [2007b] for further details.

Run	Climate	Anthropogenic emissions	Run duration
1	1990s	1990s	10.5 years
2	A2 2050s	1990s	10.5 years
3	1990s	A2 2050s	10.5 years
4	A2 2050s	A2 2050s	10.5 years
5	1990s	B1 2050s	10.5 years
6	A2 2050s	B1 2050s	10.5 years
7	1990s	1990s; A2 2050s for CH_4	1.5 years
8	1990s	1990s North America; A2 2050s Rest of world	1.5 years
9	A2 2050s	1990s;1990s biogenic emissions	5 summers (JJA)

We have performed a number of analyses to assess the relative impacts of climate change, climate-sensitive emissions, global methane, intercontinental transport, and domestic emissions on both average and peak ozone and $PM_{2.5}$. This has been done for longer time periods (those listed in Table 1) with the global model alone and for more focused time periods with the full GRE-CAPS modelling system. For more details, please see [Dawson *et al.*, 2007d; Dawson *et al.*, 2007e; Racherla and Adams, 2007b; Racherla and Adams, 2007c].

Scientific results and highlights

According to the PMCAMx sensitivity simulations, the meteorological factor that had the largest impact on ozone was temperature, which increased MDA8 ozone on average by 0.34 ppb K^{-1}. Other factors of some importance for ozone included absolute humidity, wind speed, mixing height. For $PM_{2.5}$, temperature was found to decrease average concentrations in January by -170 ng m^{-3} K^{-1} on average due to evaporation of ammonium nitrate and organic aerosol. In July, temperature led to increases in sulfate concentrations that largely offset this decrease. Other meteorological factors with significant impacts on $PM_{2.5}$ levels included mixing height, wind speed, absolute humidity, and precipitation. This activity elucidates important physical and chemical processes that link climate change to air quality, eliminates minor sensitivities from consideration, and is useful for understanding later simulations in which meteorological parameters change simultaneously.

Several conclusions result from the global-scale simulations with future climate change. The tropospheric ozone burden decreased by 5 %, primarily as a result of faster ozone loss rates via photolysis in the presence of water vapour. Ozone mixing ratios at the surface in remote areas decreased between 1 and 3 ppbv. Global burdens of $PM_{2.5}$ species decreased between 2 and 18 % because of increased wet deposition with increased precipitation. However, regional precipitation decreases and increases in chemical production of sulfate led to increased $PM_{2.5}$ concentrations in some areas. Despite the fact that the global and annual average ozone burden decreases with the increasing humidity in our future climate simulations, a more complex response occurs in polluted regions. Summertime ozone increases occur over Europe and North America, but the increase is larger over North America. The different responses can largely be attributed to isoprene in the southeastern United States. Temperature-sensitive isoprene emissions increase in the model in this area leading to stronger ozone increases than seen in other polluted areas. Second, the frequency of ozone episodes (defined as any time step in which a grid cell exceeds 80 ppbv ozone) increases in our future simulations. An analysis of 5 present and 5 future years indicates that the increased episode frequency is statistically significant with respect to interannual variability.

Future outlook

Although project results to date provide a number of important insights into future air quality under a changing climate, important issues remain. Work is ongoing at Carnegie Mellon University to refine and extend these results. Current areas of interest are to add the mercury cycle to GRE-CAPS, develop a simulation of ultrafine particle number concentrations resulting from nucleation and primary emissions, and improve the model treatment of organic aerosol chemistry and volatility.

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Interactions between Particulate Matter in the Atmosphere and Climate

A contribution to ACCENT CCAQ: Group 3

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Introduction

The Earth's climate is controlled by numerous factors. These include oceanic, terrestrial and anthropogenic emissions of trace gases and aerosol particles. Aerosol particles can influence climate relevant processes of atmosphere, ocean or biosphere, and thus the exchange between and the coupling of the different Earth System components. In the atmosphere aerosol particles from the bio-sphere and ‘anthropo’-sphere affect the radiative fluxes and act as cloud condensation nuclei (CCN) and ice nuclei (IN) and modify the micro-physical properties of clouds, with potential consequences for cloud macro-physical properties and for the formation of precipitation. In the ocean the deposition of iron containing mineral dust advected from land deserts may play a role in controlling the marine primary productivity, phosphorus transported with dust particles fertilize terrestrial vegetation. Volatile organic compounds released by plants affect atmospheric ozone concentrations and contribute to the particle load. In return, environmental properties influence cycling and properties of aerosols. For example, the production and atmospheric release of gaseous and particulate matter from natural sources (including mineral dust and seasalt) is largely controlled by temperature, precipitation and surface winds. All these interactions and feedbacks demonstrate that aerosol particles are important players in the climate system and emphasize the need for complex Earth-System models to properly address aerosol impacts on climate.

Aerosol particles affect not only climate but contribute to smog, acid rain and other health hazards. Air pollution is largely driven by the same emissions as climate change (*i.e.* traffic, energy sector, agriculture: *e.g.* CO, hydrocarbons, SO_2 and NOx emissions). Emission control for environment and climate protection requires us to quantify source attribution to specific aerosol effects by modeling. In addition, climate respectively weather controls transport and removal of pollutants as well as emissions from natural sources. Development of air quality and climate models occurred independently by different communities although the processes represented in models are the same. Both climate change and air quality models specify aerosols according to sources, both need to capture spatial and temporal subscale processes and use surface networks for evaluation. However, in the public perception air pollution is a priority issue only in numerous urban areas and, practically all megacities, whereas climate change is recognized as a global problem.

Aerosol effects on climate

Aerosol particles resulting from human activity have substantially increased the global mean aerosol burden since preindustrial times. Aerosol particles can affect the climate system via several mechanisms. Impacts are 1) the reflection of solar radiation back to space (a “direct” effect), 2) the absorption of solar radiation by soot and mineral dust to warm the atmospheric aerosol layer, which could hinder cloud formation and/or cause cloud droplets to evaporate (a “semi-direct” effect), and 3) the capability to act as condensation nuclei for (water and ice) clouds (“indirect effects”). The last effect, which is expected to increase the solar reflection of (water) clouds, is often distinguished into a cloud albedo and a cloud lifetime effect. The cloud albedo effect captures the process by which polluted clouds with more but smaller droplets appear brighter, whereas the lifetime effect considers that polluted clouds with more but smaller droplets reduce the likelihood for cloud droplets to grow to raindrop size, thereby extending the cloud lifetime. Modeling results suggest that these indirect effects are more important than the direct and semi-direct [Lohmann *et al.*, 2005; Schulz *et al.*, 2006]. However, estimates of aerosol-cloud interactions based on observations and modeling are still very uncertain. In particular, marine boundary layer and shallow convection clouds are not very well represented in climate models.

Projected climate change

Since the middle of the 19th century global mean surface temperatures have increased by almost one degree Celsius. Recent climate simulations suggest that the global mean temperatures may increase by 2.5 to 4 degree Celsius until the end of this century. Chemical transformations and the cycling of aerosol particles may mainly affected by changes in cloudiness, precipitation and solar insolation. Figure 1 shows the differences of 30-year averages of these parameters between 1961-19990 and 2071 to 2100 as calculates by the MPI Earth System Model ECHAM5-OM1 [Roeckner *et al.*, 2006].

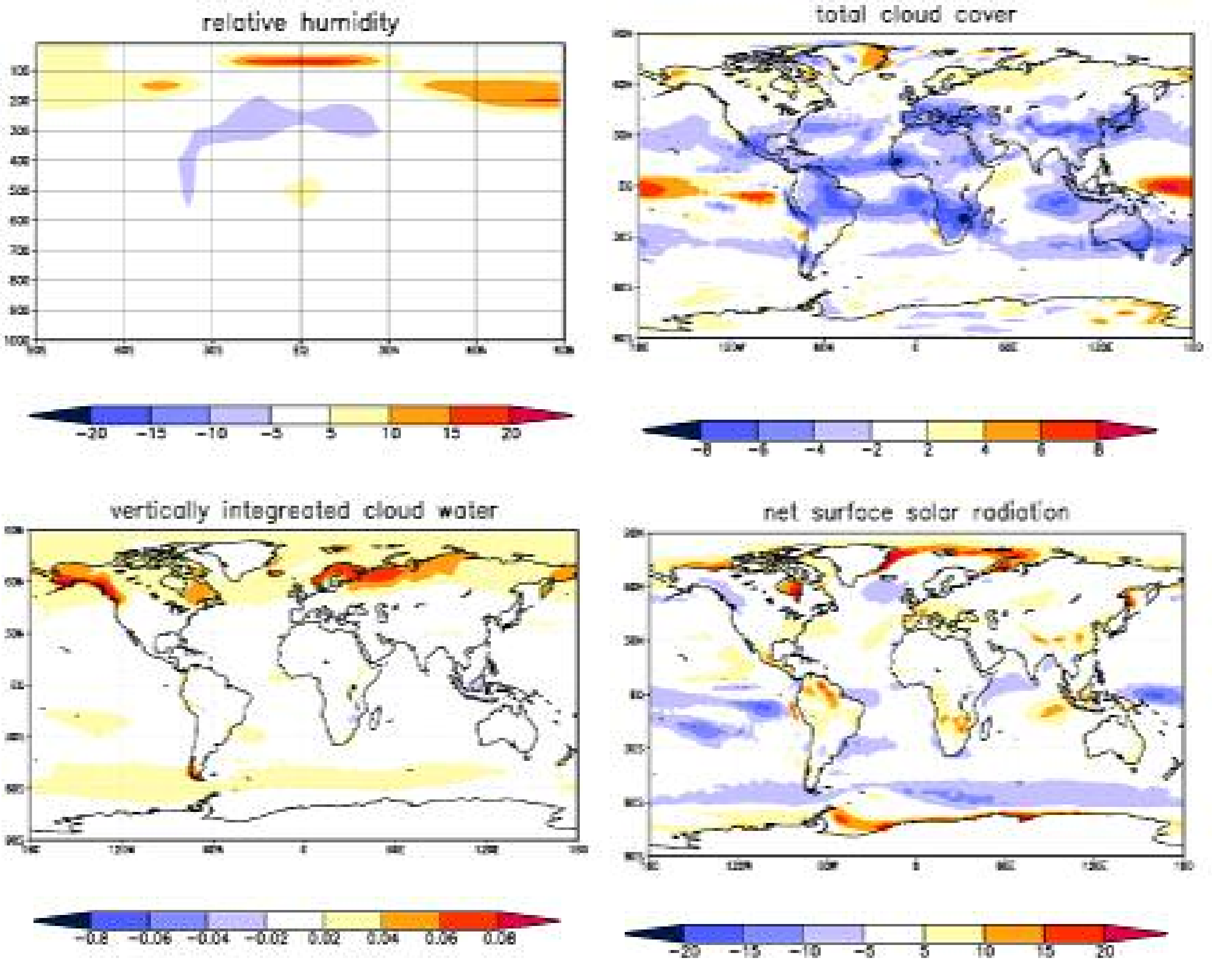

Figure 1. Model calculated differences between two 30-year averages (2071 to 2100) – (1961 to 1990) of relative humidity [%], total cloud cover [%], vertically integrated cloud water [g m^{-3}], and net surface solar radiation [W m^{-2}].

Changes in relative humidity are small because both water vapour concentration and temperature is enhanced. Clouds become optically thicker due to higher liquid water contents in a warmer climate but cloud cover decreases in low and mid-latitudes and increases in some regions of the tropics. Solar insolation at surface exhibits small increases over the continents and a decrease in high latitudes of the SH and in the tropics. The precipitation amount tends to increase in humid climate zones and decreases in arid climate zones. The length of dry spells increases worldwide. Model calculations suggest that ozone changes resulting from climate warming only are negative in a large fraction of the troposphere because of enhanced photochemical destruction by water vapour. In the tropics, increased lightning activity may lead to larger ozone concentrations [Brasseur *et al.*, 2006].

Climate induced changes of the aerosol cycles

From present day to future conditions the anthropogenic aerosol burden shifts generally from the northern high-latitudes to the developing low latitude source regions with impacts on regional climate. Atmospheric residence- and aging-times show significant alterations under varying climatic and pollution conditions. Concurrently, the aerosol mixing state changes with an increasing aerosol mass fraction residing in the internally mixed accumulation mode. The associated increase in black carbon causes a more than threefold increase of its co-single scattering albedo from 1860 to 2100. Mid-visible aerosol optical depth increases from pre-industrial times, predominantly from the aerosol fine fraction, peaks at 0.26 around the sulfate peak in 2020 and maintains a high level thereafter, due to the continuing increase in carbonaceous aerosols. The global mean anthropogenic top of the atmosphere clear-sky short-wave direct aerosol radiative perturbation intensifies to $-1.1 \mathrm{Wm}^{-2}$ around 2020 and weakens after 2050 to $-0.6 \mathrm{W\,m}^{-2}$, owing to an increase in atmospheric absorption [Stier *et al.*, 2006a].

Future dust may be 20 to 60 % lower than current dust loadings, mainly as a consequence of a climate-induced decrease in desert extent [Mahowald and Liu, 2003]. However, a decrease in desert extent is not confirmed by the most recent simulations for IPCC 4AR. In addition, models used so far do not allow interactive vegetation or dust interactions with radiation or clouds and the subsequent impact on vegetation. In the case of no change in source areas, models suggest a 20 % decrease in desert dust in the future due to changes in soil moisture and surface winds. Stier *et al.* [2006a] predict a distinct inter-annual variability and an increase of around 10 % towards the end of the integration period (2100) assuming fixed preferential source areas and year 2000 vegetation cover. Tegen *et al.* [2004] report that when taking only modern natural sources into account, projected dust emissions increase by 9 % according to the ECHAM4-driven simulation and decrease by 19 % according to the HADCM3-driven simulation. Analyses of future changes in dust emissions suggest dust emissions may increase or decrease, but either way not vegetation feedbacks but the effects of climate change will dominate dust emissions. In addition, one has to take into account that the atmospheric residence time of dust varies depending on the amount of condensable matter (OC, sulfate, nitrate) [Stier *et al.*, 2006b].

So far most model studies consider only some isolated effects. Long-term climate simulations including interactions between the terrestrial and marine biosphere, the pedosphere and the atmosphere have not been performed. Based on the present state of scientific understanding we even do not know whether feedbacks between climate and natural emissions are important or just a second order effect.

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Air Pollution and Precipitation

A contribution to ACCENT CCAQ: Group 3

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Introduction

The recent IPCC report [Solomon *et al.*, 2007] has investigated the precipitation pattern in a future climate. For Europe, an increase of precipitation in the northern European Countries is anticipated of around 20 % (in winter) while for the southern European Countries a decrease of around 20 % (in summer) is foreseen. Furthermore, an increase if extreme events is likely, including events of extreme precipitation.

In the past years, studies of Rosenfeld *et al* [2007] and others have shown that increasing particulate air pollution is decreasing orographic induced precipitation of up to 25 %, causing the loss of significant water resources.

Up to now, the two issues have not yet been combined. However, it is mandatory to study the impact of pollution on precipitation in climate change scenarios as the suppression of precipitation might add to the shortness in rain in some regions, and counteract the increase in others. Also, it will influence the foreseen increase in severe precipitation events. As water shortness can be anticipated as being one of the major issues in the future, also cloud seeding activities to counteract the precipitation reduction by pollution have to be seriously taken into consideration.

Scientific activities

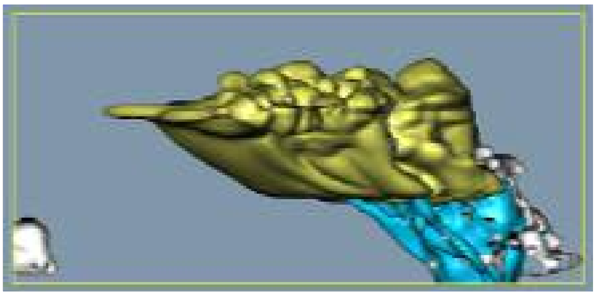
The Laboratoire de Météorologie has developed in the past years a powerful 3-D model to study in detail the interaction of particulate pollution and clouds.

This 3-D model with detailed (bin) microphysics couples the 3-D non-hydrostatic model of Clark and Hall [1991] with the Detailed Scavenging Model DESCAM [Flossmann *et al.*, 1985] A detailed description of the microphysical package, including sensitivity studies of DESCAM under mixed phase conditions can be found in Leroy *et al.* [2007a]. The microphysical model employs five distribution functions: f_{AP}, f_d, f_i, are number density distributions functions respectively for the wet aerosol particles (AP), the drops and the ice crystals and $g_{AP,d}$ and $g_{AP,i}$ account for the mass density distribution of aerosol particles inside drops and ice particles. The five functions are discretized over 39 bins that cover a range of radius from 1 nm to 6 μm for the wet AP and from 1 μm to 6 mm for the liquid or solid hydrometeors.

The microphysical processes that are considered in the model are: condensational growth and activation/deactivation of AP, condensation and evaporation of droplets, coalescence, homogeneous and heterogeneous nucleation, vapor deposition on ice crystals and riming. Droplet nucleation relies on the calculation of the activation radius derived from the Koehler equation [Pruppacher and Klett, 1997], but is also dependent on temperature as described in Leroy *et al.* [2007]. Growth rate of drops and ice crystals are given by Pruppacher and Klett [1997]. Homogeneous and heterogeneous nucleation follows respectively the works of Koop *et al.* [2000] and Meyers *et al.* [1992].

Scientific results and highlights

This model has been applied already to a number of different cases and has allowed studying the interaction of aerosol particles and clouds [Leroy *et al,* 2007b, Leroy, 2007]. In two sensitivity studies the particle number density distribution has been changed to investigate the resulting change in precipitation development. In Figure 1 a case study of the convective CRYSTAL-FACE cloud [Heymsfield *et al,* 2005] is presented.



Pollution at the surface: $N_{AP} \approx$ 400 cm^{-3}

Cloud droplets : 0.01 g m^{-3} contour in grey

Rain drops : 1 g m^{-3} contour in blue

Ice crystals : 0.01 g m^{-3} contour in yellow

Pollution at the surface $N_{AP} \approx$ 6500 cm^{-3}

Cloud droplets: 0.01 g m^{-3} contour in grey

Rain drops : 0.03 g m^{-3} contour in blue

Ice crystals: 0.01 g m^{-3} contour in yellow

Figure 1. Envelope of cloud droplets, rain drops and ice crystals in the CRYSTAL-FACE cloud. We note an increase of cloud top and a decrease in raindrop formation for the polluted case. A publication concerning this case study is under revision [Leroy *et al,* 2007].

In another study [Leroy, 2007] we have studied the precipitation in an intense precipitation event in the Cevennes region in southern France on 27th and 28th October 2004.

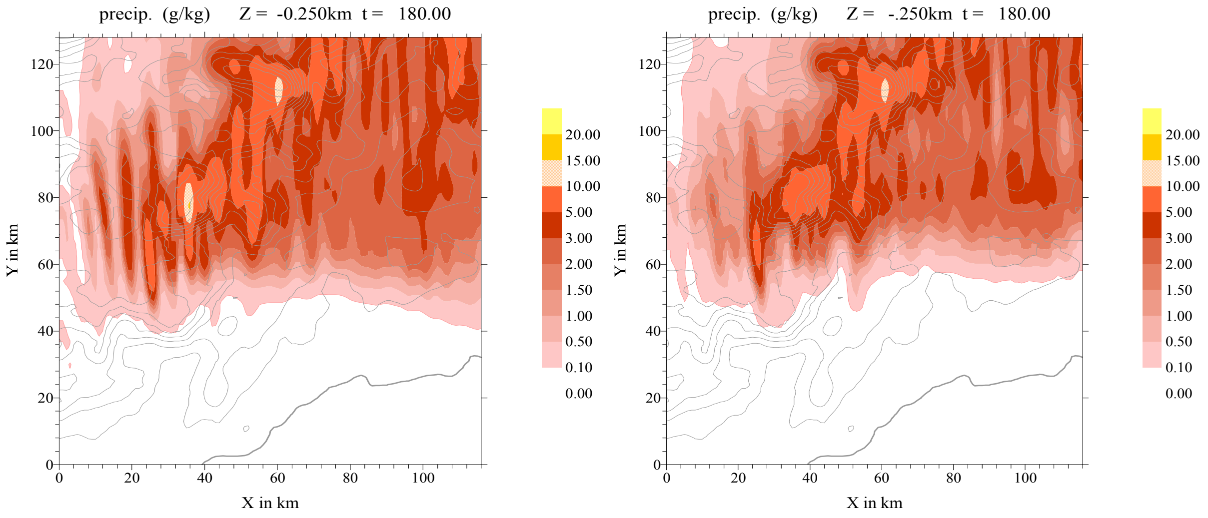


Figure 2. Cumulative rain on the ground after 180 min of simulation; left: 700 cm^{-3}, right: 2400 cm^{-3} aerosol particles at the ground.

In this case, which corresponds to medium high strato-cumulus clouds, the increase of particulate pollution resulted in a decrease of precipitation of about 15 %.

Future outlook

Our modelling studies confirm the work of Rosenfeld, Cotton [Jirek and Cotton, 2006] and others that an increase of particulate pollution can reduce the precipitation locally to up to 30 %. In contrast to most of the models used, our model is 3-D with a fully detailed treatment of the liquid, ice and particulate phase, and thus allows treating a larger range of cloud scenarios.

In the future, the particulate pollution will change. Once trends of this evolution will be known, our model can be applied not only to those pollution scenarios keeping the dynamics constant, but can be applied to pollution scenarios in a changing climate. In addition to a local modification of precipitation, a reduction in wet removal and an increase of cloud processed aerosol particles in the air is possible. Furthermore, the vertical extension of clouds if affected, modifying the venting of pollution from the boundary layer to the higher atmosphere. This will affect air quality.

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Bacteria and Clouds

A contribution to ACCENT CCAQ: Group 3

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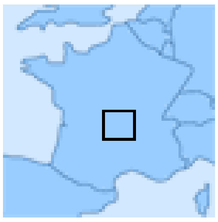
Introduction

Microorganisms disseminate through the atmosphere, spreading human, animal and plant diseases over large areas. About one third of airborne bacteria population is associated with the breathable fraction of particles ($D < 8\mu m$). Hence, most existing bodies of research on bioaerosols have focused on issues relative to health hazards. However, since recently there is an increasing interest on atmospheric fate of bioaerosols, as it has been shown that they can be subject to significant vertical and horizontal transport processes. Their presence in the troposphere allows them to affect the chemistry and physics of the atmosphere, and in turn be subject of atmospheric chemical and physical processes.

Recent studies demonstrate that bioaerosols modify the Earth's radiative budget through scattering and absorbing radiation and also through their role in cloud formation and precipitation processes. Indeed, since (bio)organic particles can be composed of polar, surface active, water-soluble, and hygroscopic compounds they can efficiently act as cloud condensation nuclei (CCN) and ice forming nuclei (IFN).



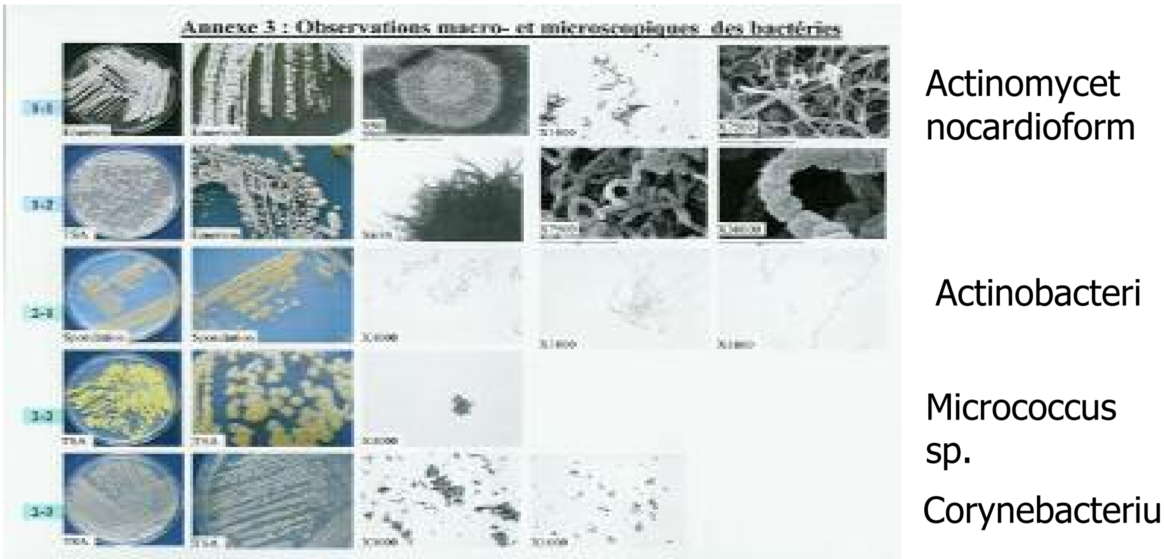
Observatoire de physique (in the foreground) on the summit of the Puy de Dôme (Massif Central) in the center of France.

Scientific activities

Since several years, the measuring site on the summit of the Puy de Dôme in the centre of France, collects cloud water and analyses it in order to determine the living organisms that it contains.

Scientific results and highlights

Below some specimen are displayed. We can note that an important number of bacteria, yeasts and fungi are found in cloud water. In addition, important concentrations of chemical species are found in cloud water that serves as nutriments. The fact that clouds remain super-cooled in the atmosphere at temperatures well below zero degree consists equally a favourable environment for these living organisms.



Future outlook

In a changing climate the ICCP report predicts an increase in global temperature. This will possibly result in an increase of bacterial activity, which is known to be temperature dependent. Thus, the known potential impact of biological particles as CCN (size) and IN (pseudomonas syr) can be affected. Equally, in the future, the fact that clouds are an ideal vector of transport for bacteria (and potentially diseases) has to be further investigated.

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Organic Aerosols in a Changing Climate

A contribution to ACCENT CCAQ: Group 3

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Introduction

Global climate change will undoubtedly affect the life cycle of atmospheric pollutants: emissions, transport and transformation and deposition patterns. This is a subject of ongoing research efforts, but at the moment the impacts of future climate change on regional air quality are far from being understood. It is of particular difficulty to speculate on future changes of regional air quality due to climate change in terms of particulate matter, given the complexity of their sources, composition and removal processes. All this said, this short contribution tries to highlight, in relation to future climate change, some issues connected to organic aerosol, a subject for which, in spite of impressive advances in recent years, our present understanding is still rather limited.

Scientific highlights

Organic aerosol (OA) components account for a large, sometimes even dominant, fraction of air particulate matter. They influence the physical and chemical properties of aerosol particles and thus have effects on the atmosphere and climate through interaction with reactive trace gases, water vapour, clouds, precipitation, and radiation [Fuzzi *et al*., 2006]. Moreover, they influence the biosphere and human health through the spread of reproductive materials and micro-organisms, impacts on respiratory and cardiovascular functions, as well as allergic and infectious diseases (Figure 1).

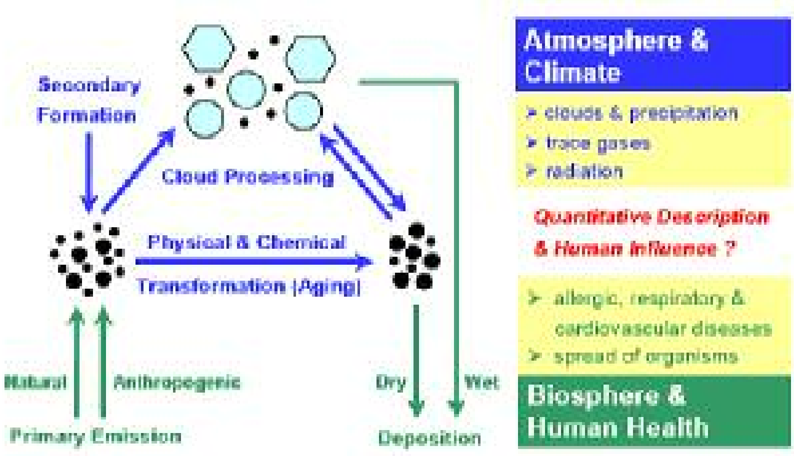

Figure 1. Atmospheric cycling of organic aerosols and effects on the climate system and human health [Pöschl, 2005].

At present our understanding of OA composition, physical and chemical properties, sources, transformation and removal characteristics is very limited, and estimates of their actual environmental effects are highly uncertain. Figure 2 illustrates the interdependencies between aerosol sources and formation, composition and properties, interactions and transformation, climate and health.

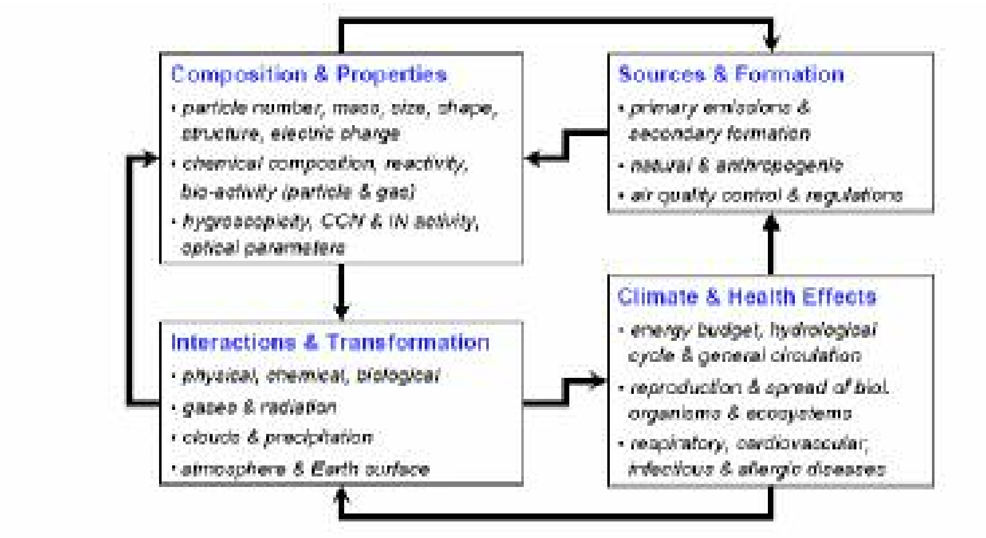

Figure 2. Interdependencies and feedback loops between atmospheric aerosol sources and formation, composition and properties, interactions and transformation, and climate and health effects [Pöschl, 2005].

Obviously, the resulting feedback loops are of central importance for the science and policy of air quality and global change. Thus a comprehensive characterization [climatology] and mechanistic understanding of particle sources, properties, and transformation is required for quantitative assessment, reliable prediction, and efficient control of natural and anthropogenic aerosol effects on climate, air quality and public health.

Regional and local air quality is significantly influenced by weather patterns and variability and also the spatial patterns of emissions. Climatic change will clearly affect both these parameters [Meleux *et al*., 2007]. In particular, the IPCC Fourth Assessment Report [IPCC, 2007] concludes that in the whole range of emission scenarios considered, a global warming trend of 0.2 °C per decade is projected for the next two decades and that, at least, a further warming of about 0.1 °C per decade would be expected thereafter.

There are at present no data to quantitatively assess the effect of climate change on the lifecycle of OA, but in qualitative terms it can be speculated that in a warming climate trend, the sources of organic aerosols are likely to be affected.

The global sources of organic aerosols can, in broad terms, be listed as:

biomass burning;

fossil/bio fuel;

primary biogenic;

secondary biogenic (BSOA); and

secondary anthropogenic (ASOA).

The strength of all these sources is known with a large uncertainty; very little is still known on primary biogenic sources. Among these sources of OA, an increase in temperature will affect to a greater extent biogenic and secondary emissions, due to the sensitivity of both biological and chemical conversion processes to temperature.

Primary biogenic sources of OA

Proteinaceous living and non-living material derived from terrestrial and marine ecosystems has been detected in atmospheric aerosols, but a global source function is not available. These biogenic primary particles may act, among other effects, as cloud condensation nuclei and ice nuclei and are frequently found within cloud droplets [Fuzzi *et al*., 1997; Amato *et al*., 2007].

On the other hand, O'Dowd *et al.* [2004] observed that in the North Atlantic region during periods of high biological activity an average 45 % of the submicron aerosol mass is accounted for by insoluble primary organic particles, while during winter, when biological activity is at its lowest, the OA contribution to total aerosol mass decreases to a few percent. No evaluation can however be made from these data of a global strength of this marine source.

Recently, Jaenicke [2005] estimated that the primary biogenic particles emission from the biosphere may amount to *ca.* 1000 Tg/year. On the other hand, Elbert *et al.* [2007], from experimental data collected in Amazonia, estimated the global emission of fungi alone to account for ca. 50 Tg/year.

Irrespective of the fact that all the above figures are highly speculative, biologically-mediated emissions are expected to be highly sensitive to a global temperature increase.

Secondary organic aerosol [SOA] sources

Volatile organic compounds (VOC) of both natural (BVOC) and anthropogenic (AVOC) origin are converted in the atmosphere to secondary organic aerosol, BSOA and ASOA, respectively [Kanakidou *et al*., 2005]. Their global source is highly uncertain and estimations span from 12-70 Tg/year [Kanakidou *et al*., 2005] to 510-910 Tg/year [Goldstein and Galbally, 2007].

In addition, from current model estimates [Kanakidou *et al*., 2005], about 90 % of SOA is believed to be BSOA. However, new results have recently reported that much more SOA are measured in urban environments than models are able to predict, and that this excess SOA are produced from the oxidation of AVOCs [Volkamer *et al*., 2006]. Extrapolating these field experimental results to the global scale, an additional 3-25 Tg/year ASOA would be produced globally. In addition, ASOA production from the oxidation of semi-volatile primary OA has been demonstrated in polluted environments, causing a further increase of ASOA production [Robinson *et al*., 2007].

All the above mentioned processes involved in SOA production (precursor BVOC emissions, volatility of primary anthropogenic OA, photochemical oxidation) are clearly temperature-dependent and are therefore susceptible of changes in a warming climate.

Conclusions and outlook

The research on the effects of global climate change on regional and local air quality has only recently been initiated and very little results have as yet been produced. Even more so, concerning the possible changes of aerosols in a changing climate, due to the inherent complexity of the aerosol cycle. This short contribution is intended for highlighting, in a qualitative way, an important component of atmospheric aerosol, the organic one, which, due to its very nature, can potentially be affected by a warming trend of climate. It should be underlined that to constrain the processes briefly described above and the possible future changes a strong continuing research effort is important.

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Need for Improved Standardization of Aerosol Species in Optimized Observation Strategies: First Results from EUSAAR I3 Project

A contribution to ACCENT CCAQ: Group 3

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Summary

Future needs for a well suited strategy for observing atmospheric composition changes and have to be addressed to meet the scientific challenges ahead resulting from climate change. The new EU-funded Infrastructure initiative EUSAAR (European Supersites for Atmospheric Aerosol Research) is aimed at improving the availability of advanced aerosol parameters of interest to Air quality and climate studies. First results from EUSAAR networking activities showed that standardization will be required to improve the functionality of aerosol monitoring networks and provide high quality data required for measuring future composition changes in the atmosphere.

Introduction

Future needs for a well suited strategy for observing atmospheric composition changes and have to be addressed to meet the scientific challenges ahead resulting from climate change. Atmospheric aerosols are amongst the most sensitive species to climate change not only because emission rates of both primary particles and gaseous precursors of secondary particles are expected to change, but also because the formation rates of secondary particles is highly dependent on environmental conditions. Because aerosols are of great importance because of their impact on human health, visibility, continental and maritime ecosystems, or the Earth's climate, there is a clear requirement to develop and optimize dedicated monitoring of their concentrations and properties at the global scale. Aerosol impact on climate is in fact repeatedly mentioned as one of the most uncertain aspects of climate change, and their impact on human health is a growing matter of concern. The aerosol monitoring strategy should contribute to understand regional to intercontinental transport of aerosols in order to design efficient policies for monitoring of aerosols and their precursors and emission abatement strategies.

Scientific activities

Aerosol observational data are currently available from European monitoring (*e.g.* EMEP / GAW) networks and within regional, national and international projects. However, the vast majority of information arises from stations located in urban centres and this information is often limited to regulated parameters as PM_{10} or $PM_{2.5}$. The present situation is, therefore, clearly not sufficient in the context of an integrated atmospheric observing system for air quality and climate studies. The new EU-funded Infrastructure initiative EUSAAR (European Supersites for Atmospheric Aerosol Research) is aimed at improving the availability of advanced aerosol parameters of interest to Air quality and climate studies. Through its 6 networking activities, EUSAAR, will provide easy access to high quality data bases and will promote standardised measurement protocols, intercomparability of observations and quality assurance common to all research sites in Europe. In particular, one priority within the EUSAAR program is to address the homogeneity of aerosol physical, chemical and optical properties measured in a network of 20 supersites over Europe.

Scientific results and highlights

This has been a clear priority of the EUSAAR partner over the first period of activity. First results of intercomparison highlighted the crucial needs for:

1. improved standardization of thermo-optical analytical procedures for OC + EC analysis: round-robin intercomparison confirmed previous work performed within EMEP showing EC/OC variability higher than 25 % between the different partners involved in aerosol chemistry determination (see Figure 1)

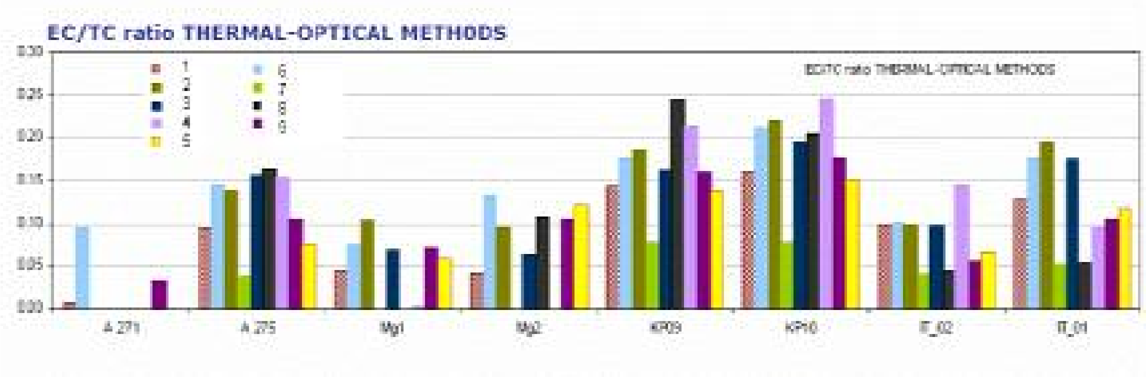

Figure 1. Round-robin intercomparison of EC/TC measurements from 9 EUSAAR research partners using filters collected at 4 different EUSAAR sites

2. a standardized artefact-free procedure for determining particulate organic and elemental carbon, validated for all kinds of sites Europe: very few observing stations are currently capable of providing estimates for positive and/or negative artefacts for their OC measurements while estimated performed within EUSAAR confirmed that these artefacts can be extremely high (more than 50% of the measured OC concentration)
3. a better standardisation of measurements of physical aerosol parameters: intercomparisons of aerosol size spectrometers in use at supersites shows large variability of concentration and size when measuring identical aerosols.
4. a better assessment of the intercomparability of Apparent Black Carbon measurements performed by different type of instruments commercially available
5. a better assessment of the intercomparability of diffusion coefficient measurements performed by different type of instruments commercially available

Future outlook

A first conclusion from the work performed within EUSAAR is therefore that a global observing strategy should optimized standardization of in-situ measurements of atmospheric species of interest to climate change and air quality studies. This is especially true for aerosol measurements but may also be the case for many aerosol precursors in the gas phase. Without a rapid implementation of EUSAAR-like research project at a larger scale, in-situ measurements may not provide adequate information for documenting trends in atmospheric composition, validation of remote sensing results and chemical-transport models for improving air quality forecast. The implementation of standardized and more automatic protocols for the production of an advanced aerosol data base accessible to users is an important step towards full functionality of an integrated global chemistry observation system in particular for providing high quality climate and air quality relevant data.

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Global-scale Dust Transport: Can We Detect the Impact of Climate Change and Land Use?

A contribution to ACCENT CCAQ: Group 3

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Introduction

Mineral dust particles, lifted by winds from soils, are believed to play an important role in global climate processes. Dust particles modify the radiative processes in the atmosphere, reducing insolation at the Earth's surface and producing heating aloft. These processes would tend to increase atmospheric stability and affect a wide range of atmospheric processes [Perez *et al.,* 2006]. Dust particles could also affect changes in cloud properties through cloud microphysical processes [Rosenfeld *et al.,* 2001]. Dust is also believed to impact climate through the carbon cycle by modifying primary productivity in the oceans. Large regions of the ocean contain abundant concentrations of primary nutrients - nitrogen and phosphorous species essential for phytoplankton growth - yet productivity remains low because of the lack of iron, an essential micronutrient. The deposition of dust, which typically contains several percent iron, could stimulate biological production which, in turn, would draw down CO_2 from the atmosphere. Thus, through these various processes, changes in the generation and transport of dust could serve to modulate climate [Jickells *et al.,* 2005; Mahowald *et al.*, 2005]

In this paper I address two factors that could affect dust generation and transport. The first is climate change itself. How do dust sources respond to changes in climate? The second has to do with the role of humans in modulating dust transport. Is there any evidence that land use has affected dust transport on a global scale?

Dust generation is dependent on many factors. In a recent study of global dust sources [Prospero *et al.*, 2002] three characteristics were common to the most active dust sources:

1. they were located in arid regions;
2. they were located in topographical lows or adjacent to high-lands; and
3. they were flooded in the Pleistocene or Holocene.

The first characteristic is a climate issue - common experience shows that dust is associated with aridity. Thus we might expect that dust generation and transport will change with changes in the distribution and amounts of rainfall amounts. The second and third concern geomorphology - the availability of large quantities of fine-grained alluvial soils which could serve as the source of particles that could be lifted by winds. Thus decreases in rainfall could lead to drying-out of alluvial deposits that are potentially rich dust sources; conversely, increased rain would increase vegetation growth that would stabilize soils and decrease erosion.

There are other geomorphological characteristics that can come into play. One is the impact of land use - land disturbance, especially agriculture and the grazing of animals, can greatly increase the erodability of soils. Land-use is a critical issue in marginal climate zones. The classical example is the "Dust Bowl" of the 1930s in the American

Midwest, a region long known to be subject to climate shifts but which was nevertheless intensely developed for agriculture during a wet phase. In light of the fact that alluvial soils are best suited for agriculture, climate change could bring shifts in rainfall that would bring aridity to areas that are now intensely cultivated.

While we have a general understanding of how dust might change with climate, there is little quantitative evidence that would enable us to project into the future. Thus these two questions address vital issues.

How does dust transport change with climate?

Dust measurements have been made in the trade winds in Barbados, West Indies [13.17 °N, 59.43 °W] since 1965 [Prospero and Lamb, 2003], yielding the longest quantitative dust aerosol record in existence. These data show that dust concentrations in the western Atlantic Trade Winds have been closely linked to climate in Africa. Dust concentration increased sharply in the late 1960s and early 1970s with the onset of drought in northern Africa. Dust concentrations have remained high on Barbados in the ensuing decades, modulated by the varying degrees of drought in the source regions.

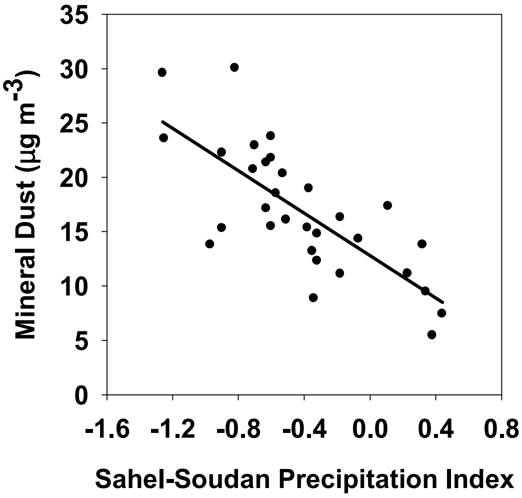

Figure 1. Scatter plot of Barbados May-September mean dust loads for the period1965 to 1998 against the Sahel-Soudan Precipitation Index (SSPI) [Prospero and Lamb, 2003]. Rainfall data are from a network of 20 stations in the Sahel-Soudan, a semiarid region between 11°-18° N extending from the Atlantic coast through northern Senegal, southern Mauritania, Mali, Burkina Faso, Niger, Chad, and into the Sudan. The SSPI is comprised of yearly averages of the normalized April-October departures expressed as standard deviations from the 1941-2001 mean.

On a year-to-year basis, dust concentrations on Barbados are linked to rainfall in the Sahel-Soudan region as shown in Figure 1 for the period 1965 to 1998. Although this study links dust to rainfall, it does not necessarily prove that rain itself is the controlling factor [Prospero and Lamb, 2003]. Other meteorological factors associated with rainfall variability could play a factor including increased winds or wind gustiness and decreased wet removal because of decreased precipitation. Indeed, it is notable that the years with the maximum dust amounts were years when a major El Niño occurred [Prospero and Lamb, 2003]. The Barbados record of increased dust transport is supported by other lines of evidence from Africa that show increased dust mobilization. These include the increased frequency of dust storms in north Africa [Goudie and Middleton, 1992], decreased visibility over large areas of northern Africa [Mbourou *et* *al.,* 1997] and the increased frequency of African dust deposition events in Alpine snows [Maggi *et al.*, 2006].

Does land-use affect dust mobilization on global scales?

The Barbados time series (Figure 2) over the period 1965 to 2004 does not show any clear long-term trends in dust transport since the onset of the dusty period in the early 1970s when drought began. The interpretation of our results - the absence of a long term trend *vis-a-vis* increased land-use - is unexpected in light of the great population growth in the Sahel region in recent decades. In the countries that span the Sahel (Chad, Niger, Burkina Faso, Mali, Mauritania, Senegal, Gambia and Guinea-Bissau) the population grew from 22 million, of which 20 million were rural, in 1960 to 42 million, 31 million rural, in 1990. By 2020, it is projected to reach 83 million, 44 million rural [Cour, 2001]. In addition to showing strong population growth, these statistics reflect a massive migration to cities [Olson *et al.,* 2005]. This same conclusion is reached by various remote sensing studies that suggest that the observed changes could be attributed to human factors such as changing land-use patterns [Hermann *et al.,* 2005]. However the interpretations of these trends, or the lack of them, are complicated by a wide range of issues including the absence of good data from the source regions and the changes in population and agricultural-husbandry practices made in response to the drought.

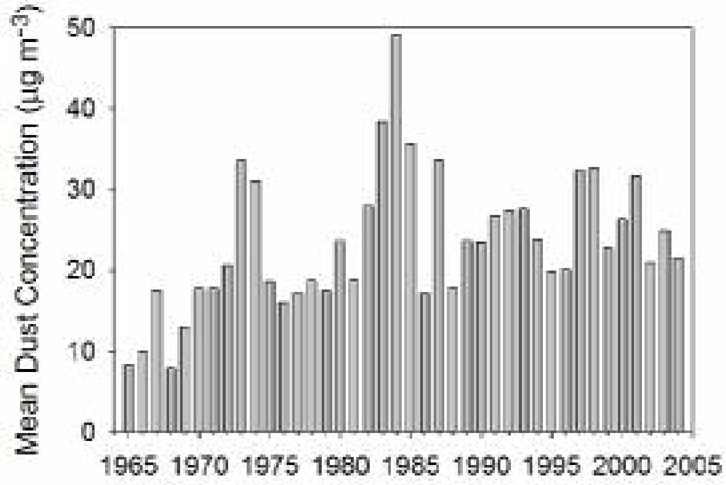

Figure 2. Barbados mean summer dust concentrations over the period 1965 - 2004.

Nonetheless recent studies of rainfall patterns and satellite vegetation indices yield a mixed picture of trends in the region. Increased rainfall and vegetation are seen in some areas, especially the Soudan, whereas in others, notably the Sahel, drought continues [Nicholson, 2005; Heumann *et al.*, 2007]. Nonetheless there are signs of a growing vegetation trend in the Sahel. Indeed, an entire issue of the Journal of Arid Environments focuses on "The Greening of the Sahel" [Hutchinson *et al.,* 2005]. Although there is still debate about the interpretation of satellite vegetation indices, there is considerable evidence that vegetation has been increasing since the height of the drought in the early 1980s. It is suggested that the landscape is reaching a new equilibrium with the climate - that the new growth reflects the spread of vegetation that is better adapted to the more arid climate along with changing land-use patterns [Hutchinson *et al.,* 2005].

Summary and conclusions

It is difficult to reach a clear conclusion about the impact of climate change and land use on dust mobilization. There are many interlocking physical, biological, economic, and social factors that come into play over various time scales. In this regard it is notable that in recent years the clear link between rainfall in the Sahel and Barbados dust, depicted in Figure 1, has become less clear. Figure 1 is based on data from 1965 to 1998. When we add data for the period 1999 to 2005, we obtain a very wide scatter. We do not understand the cause for the breakdown of the strong correlation that we have observed for over 30 years.

Unfortunately there is very little long-term dust data that can be used provide obtain a better sense of the importance of the various factors that affect dust generation and transport on global scales. Furthermore many of the World's most active dust sources are in regions that are sparsely populated and poorly linked to the larger social-economic structure. Thus, even if we did have adequate dust measurement data in the form of long time series, it would be difficult to quantitatively link these data to human factors. Such information is essential if we are to establish functional relationships between future climate change and land-use practices and socio-economic policy [Warren, 2005].

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Changing Optical Properties of Aerosols due to Different Emission Pattern Scenarios

A contribution to ACCENT CCAQ: Group 3

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Summary

Due to warmer climate and changes in emission patterns, it is expected that biogenic emissions will increase, and hence their contribution to secondary organic aerosol (SOA) mass. Recent studies have shown that that complex organic matter prevalent in SOA and primary pollution particles from biomass burning and pollution have substantially different optical properties, especially the absorption part of the refractive index. This will directly impact the effects of aerosol on visibility and heat spells.

Introduction

Aerosols impact global and local air quality by various ways. One of the direct effects of aerosols is through the interaction with solar radiation which can be scattered and absorbed by aerosol particles.[Solomon*, et al.*, 2007] The absorption of solar radiation depends on the complex refractive index and hence the chemical composition of the particles.[Bohren, 1983] Absorption by absorbing aerosols may have substantial heating effects, which can amount to 50 % of that due to warming due to greenhouse gases.[Ramanathan, *et al.*, 2007] Organic aerosols, either primary or SOA are a large component of the atmospheric aerosol loading, especially in urban environments. [Tsigaridis and Kanakidou, 2007; Tsigaridis, *et al.*, 2006] They are dominated by biogenic emissions in terms of mass,[Tsigaridis and Kanakidou, 2007; Tsigaridis, *et al.*, 2006] but the contribution to the absorbance in the atmosphere is not yet constrained. High molecular weight organic compounds that are either directly emitted (biomass burning or combustion) or form *in-situ* in the atmosphere (SOA) absorb solar radiation below about 400 nm. Hence, they contribute substantially to atmospheric absorption. The contribution of light absorbing organic compounds, such as humic like substances (HULIS) to aerosol scattering and absorption is among the largest uncertainties in assessing the direct effect of aerosols on climate. Using a cavity ring down aerosol spectrometer (CRD-AS), the complex index of refraction of aerosols containing HULIS extracted from pollution, smoke, and rural continental aerosols was measured at 390 nm and 532 nm.[Dinar, *et al.*, 2008] At both wavelengths, HULIS extracted from pollution and smoke particles absorb more than HULIS from the rural aerosol (see Figure 1).

Sensitivity calculations for a pollution type aerosol containing ammonium sulfate, organic carbon (HULIS), and soot suggests that accounting for absorption by HULIS leads in most cases to a significant decrease in the single scattering albedo and to a significant increase in aerosol radiative forcing efficiency, towards more atmospheric absorption and heating, This indicates that HULIS in addition to black carbon in biomass smoke and pollution aerosols can contribute significantly to light absorption in the ultraviolet and visible spectral regions. However, the absorption due to the rural HULIS is substantially lower, indicating that the more biogenic HUILIS absorb less and hence their main climatic effect is via scattering of solar radiation.

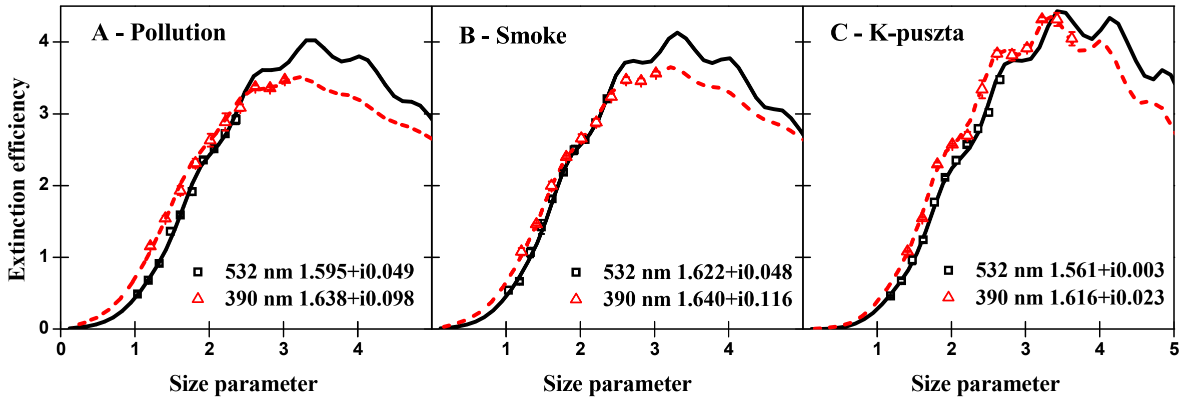

Figure 1. The extinction efficiency (Q_e) as a function of size parameter (x) as measured for HULIS samples at 532 nm (ς) and 390 nm (△). The lines are the Mie curves using the retrieved complex refractive.

Scientific results and highlights

The main results of this study with respect to air quality is that reducing the emission of smoke and of pollutants from low quality engines or diesel will substantially reduce the absorption in the atmosphere due to organic aerosol. This will directly impact visibility, cloud formation and regional heating. All of these are directly and indirectly related to air quality.

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Transport and Transformation of Pollutants (T&TP)
Access to Emission Data, Access to Laboratory Data,
Aerosols, Remote Sensing from Space (AT2),
BIAFLUX, Modelling

AT2

BIAFLUX

13 Contributions from Group 4 Participants

Building observation and modelling systems to cope with the interactions of air quality and climate change

Relation of Atmospheric Humidity and Cloud Properties to Near-surface Temperatures derived from GOME Satellite Observations

A contribution to ACCENT CCAQ: Group 4

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Summary

Cloud climate feedback constitutes the most important uncertainty in climate modelling, and currently even its sign is still unknown. In the recently published report of the intergovernmental panel on climate change (IPCC), from 20 climate models 6 showed a positive and 14 a negative cloud forcing in a doubled CO_2 scenario [Solomon *et al.,* 2007]. The radiative budget of clouds has also been investigated by experimental methods, especially by studying the relation of satellite observed broad band shortwave and longwave radiation to sea surface temperature [Ramanathan *et al.,* 1989]. Here we present results from UV/vis satellite observations of the backscattered radiance and the O_2 absorption, from which information on the dependence of cloud cover and cloud top height on surface-near temperatures can be derived. In addition, also the total atmospheric water vapour column is retrieved. We find that over most parts of the globe, an increase in surface-near temperature is connected with an increase of cloud top height and decrease of cloud cover (except the Tropics). These findings indicate a positive cloud climate feedback. Also for atmospheric humidity a positive feedback is found for almost the whole globe. Climate models should aim to reproduce our findings to reduce uncertainties in climate change predictions. Our findings might also have implications on future atmospheric chemistry: if increasing temperatures due to climate change would cause increased atmospheric humidity and reduced cloud cover, this should result in an increased atmospheric OH concentration.

Introduction

Clouds have a strong impact on both, the short-wave solar radiation and on the outgoing thermal radiation. If cloud cover increases, less solar radiation reaches the ground, but also more thermal radiation from the surface will be trapped in the atmosphere. Both effects influence the surface-near temperature with opposite signs, and their net effect depends on various cloud properties, especially on the cloud altitude [Stephens, 2005; Cess *et al.,* 1992; Hartmann *et al.*, 2001]. Today, the magnitude, and even the sign of cloud feedback is still not known (see the IPCC 4th assessment report [Solomon *et al.*, 2007] and references therein). In this study we investigate the climate feedbacks due to clouds and water vapour for fixed locations on a global scale using correlation analyses of monthly anomalies of cloud fraction, cloud top height (derived from the atmospheric O_2 absorption), and atmospheric humidity with those of the surface-near temperature. The cloud and water vapour data is derived from 7.5 years of observations of the Global Ozone Monitoring Experiment (GOME) on board the European research satellite ERS-2. We relate the GOME results to surface-near temperature observations for the same period (surface temperature data are obtained from the Goddard Institute for Space Studies [Hansen *et al.,* 2001; Reynolds *et al.,* 2002] (GISS, see http://www.giss.nasa.gov/data/update/gistemp/).

GOME on ERS-2

The GOME instrument aboard the European research satellite ERS-2 measures sunlight reflected from the Earth's atmosphere and surface covering the wavelength range between 240 and 790 nm with moderate spectral resolution [Burrows *et al.,* 1999] (0.2-0.4 nm FWHM). The satellite operates in a nearly polar, sun-synchronous orbit at 780 km altitude with an equator crossing time of approximately 10:30 a.m. local time. This has to be taken into consideration for the interpretation of our results, which might be only representative for mid-morning because of the diurnal variation of clouds [Bergman and Salby, 1996]. The ground pixels cover an area of 320 km east to west by 40 km north to south. Simultaneous to the spectral channels, also broad band intensities are measured by the so called polarization monitoring devices (PMD). Compared to the spectral channels, they have a much finer spatial resolution of 20×40 km². The Earth's surface is entirely covered within 3 days.

Data analysis

Here we analyse three products retrieved from GOME observations: the total column precipitable water, the effective cloud fraction, and cloud top height. The effective cloud fraction [HICRU, Grzegorski *et al.,* 2006] is based on broad spectral measurements with a high spatial resolution. In addition, the absorptions of water vapour and oxygen are analysed using Differential Optical Absorption Spectroscopy [DOAS, Platt 1994]. Details on the spectral analysis can be found in Wagner *et al.*, [2006]. From the retrieved absorptions of H_2O and O_2, the total column of atmospheric water vapour is derived. From the effective cloud fraction and the O_2 absorption also information on the cloud top height is derived. For this purpose, we apply radiative transfer modelling using our Monte Carlo model TRACY-2 [Deutschmann and Wagner, 2006; Wagner *et al.*, 2007]. From the three quantities (effective cloud fraction, cloud top height and total water vapour column) as well as the surface-near temperature, we calculate monthly averages. Finally, from these monthly averages, anomalies for individual months are derived (deviation from the mean value of the respective month for all years). Using these monthly anomalies we performed correlation analyses of the three quantities versus surface near temperatures.

Results

The results of the correlation analyses are shown in Figure 1. For the effective cloud fraction (top) we find decreasing values with increasing surface-near temperatures for most parts of the globe, except over the tropical oceans close to the equator. These findings are in good agreement with those of Bony *et al.* [1997], who found a negative correlation of CF (and cloud optical depth) for surface-near temperature < 26 °C and a positive correlation for surface-near temperature > 26 °C. For the cloud top height (middle), we find increasing values with increasing surface-near temperatures. Very strong changes in CTH are found over the tropical oceans close to the equator. Again our findings are in good agreement with those of Bony *et al.* [1997], who found a weak positive correlation < 26 °C and strong positive correlation > 26°C. Also Larson and Hartmann [2003] found an increasing cloud top height of tropical clouds for increasing surface-near temperatures. They found in particular that over tropical oceans, the frequency of situations with large scale uprising air and high clouds increases strongly for surface temperatures > 26 °C.

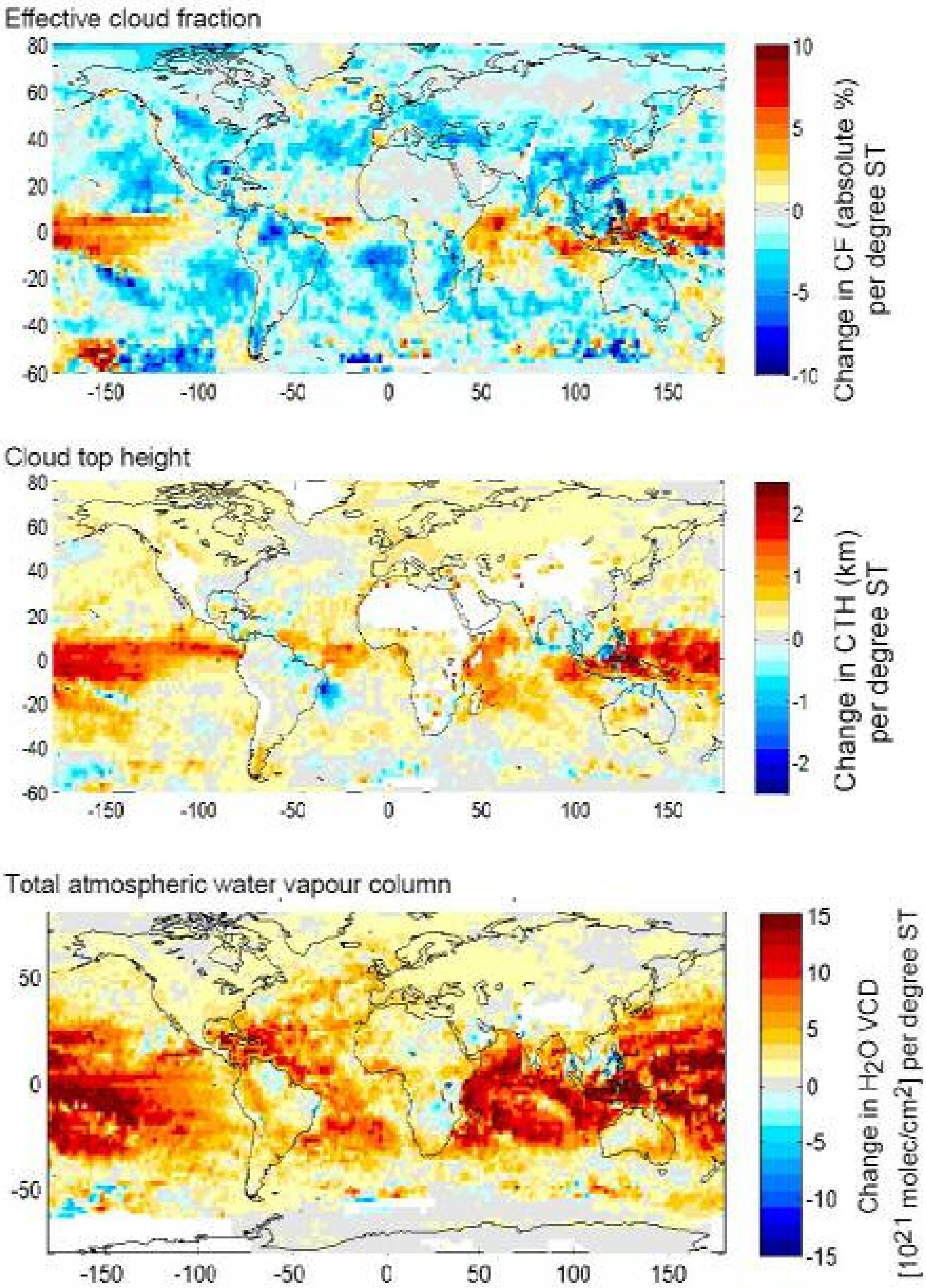

Figure 1. Dependence of cloud fraction (top), cloud top height (middle) and total atmospheric water column (bottom) on surface temperature (ST) as derived from the correlation analysis.

For the total atmospheric water vapour column, we find and increase with increasing surface-near temperatures for almost the whole globe. This dependence is expected from the Clausius-Clapeyron relationship and leads to a positive water vapour feedback [Wagner *et al.* 2006].

Conclusions

The observed dependencies of the cloud fraction, cloud top height, and the total atmospheric water vapour column on surface-near temperatures can be used to derive information on the respective climate feedbacks. For water vapour, a clear positive feedback is observed: if temperature rises, also atmospheric humidity increases. Since water vapour is the most important atmospheric greenhouse gas, this leads to an increase of the greenhouse effect. Especially for the tropics, a rather strong water vapour feedback is found [Wagner *et al.*, 2006]. For the interpretation with respect to cloud climate feedbacks, the general dependencies of cloud forcing have to be considered. Cloud forcing depends on many factors, in particular on cloud optical depth, cloud top height; it varies also with latitude. In a simplified way, this can be summarized as follows:

a) clouds tend to heat (cool) the atmosphere at low (high) latitudes compared to clear skies [Stephens, 2005; Ramanathan *et al.*, 1989; Harrison *et al.*, 1990].

b) cloud heating increases with increasing cloud top height [Stephens, 2005; Cess *et al.*, 1992; Kubar and Hartmann, 2007].

Based on these dependencies, the observed changes of cloud fraction with increasing surface temperature can in general be interpreted as a positive cloud feedback: at high latitudes the decrease in cloud fraction will lead to a reduced cooling; at low latitudes over the oceans, the increase in cloud fraction will increase the heating. In addition to the effect of changing cloud fraction, also the increase of cloud top height will increase the cloud heating and can be interpreted as an additional positive cloud feedback. It should, however, be taken into account that these simplified conclusions might not be true for individual cases. More detailed information on these complex interactions can (and should) be gained from the comparison of our results to model simulations.

Our findings might also yield information on future atmospheric chemistry under climate change conditions: if for most part of the globe atmospheric humidity increases and cloud cover decreases, this should result in an increased atmospheric OH concentration.

Acknowledgements

We like to thank the European Space Agency (ESA) operation center in Frascati (Italy) and the “Deutsches Zentrum für Luft- und Raumfahrt” (DLR, Germany) for making the ERS-2 satellite spectral data available. Surface-near temperature data are from the Goddard Institute for Space Studies (GISS) [Hansen *et al.,* 2001; Reynolds *et al.,* 2002], http://www.giss.nasa.gov/data/update/gistemp/.

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Coupled Climate, Chemistry, Ecosystem Modelling for Assessing the Interactions between Air Quality and Climate Change

A contribution to ACCENT CCAQ: Group 4

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Introduction

Often the air quality modelling and climate modelling communities work as two separate disciplines. Historically climate models did not include any treatment of atmospheric pollutants. Radiatively active gases such as CO_2 were prescribed as single globally-averaged numbers, whereas ozone was often prescribed as a two-dimensional (latitude and height) field. This works fine for relatively well-mixed species, but was not appropriate when climate scientists wanted to include the effects of aerosols. Sulphate aerosols were the first pollutants to be simulated interactively in climate models. Climate centres that submitted climate model results to the IPCC 4th Assessment Report all included interactive aerosols with varying degrees of sophistication, but no interactive radiatively active gaseous species. Many climate centres are planning to include interactive gaseous species in time for the IPCC 5th Assessment.

Air quality modelling generally started with offline modelling. Here chemistry transport models (CTMs) read in meteorological variables (such as winds and temperatures) from an archive to advect and chemically process chemical species. The time frequency of these archived variables can vary from hourly to daily. These archives came from forecast or climate GCMs. As the CTMs became more sophisticated they needed more variables than winds and temperature, such as convective fluxes. One way around this is to embed the chemistry in the GCM. This enables the chemistry scheme to access all the meteorological variables necessary at the frequency of the GCM timestep (typically 5 minutes in mesoscale models to 30 minutes in climate models). Hence the climate communities and air quality communities are converging on the need for coupled chemistry GCMs.

Climate-chemistry-ecosystem coupling.

The importance of the link between chemistry and ecosystems has been long established. The emissions of isoprene from vegetation [Guenther *et al.* 1995], NO_X from soils [Yienger and Levy 1995] and methane from wetlands [Aselmann and Crutzen 1989], are widely used in tropospheric chemistry models. These emissions can be dependent on meteorological variables such as temperature, insolation and precipitation, but also on ecosystem variables such as soil and vegetation amounts and types. In a future climate, these meteorological and ecosystem variables are likely to have changed considerably [Cox *et al.* 2000] leading to significantly different natural emissions than measured today [Sanderson *et al.* 2003a, Gedney *et al.* 2004]. Thus changes in natural emissions need to be taken in to account when predicting future atmospheric composition and air quality.

As well as being a source, ecosystems are also a sink for many trace gases through dry deposition to vegetation and soil [Wesley 1989]. The deposition velocities of species depend on the type of vegetation and soil, and also on meteorologically influenced parameters such as the leaf and soil moisture [Sanderson *et al.* 2003b] and the opening of stomata on the leaf's surface. Uptake through plant stomata is an important mechanism for removing ozone from the atmosphere [Ashmore 2005].

The opening of plant stomata is determined by meteorological factors including the, the atmospheric concentration of CO_2 and the water stress of the plant. Both these factors are likely to change in a future climate.

In Sanderson *et al.* [2007] we coupled an atmospheric chemistry model (STOCHEM) to the Met Office Hadley Centre climate model which includes a land surface exchange scheme to investigate the impact of changes in plant stomata on surface ozone concentrations. The impact on surface ozone of doubling CO_2 concentrations is shown in Figure 1. The largest impact was found in the boreal spring where European surface ozone concentrations increased by up to 6ppb.

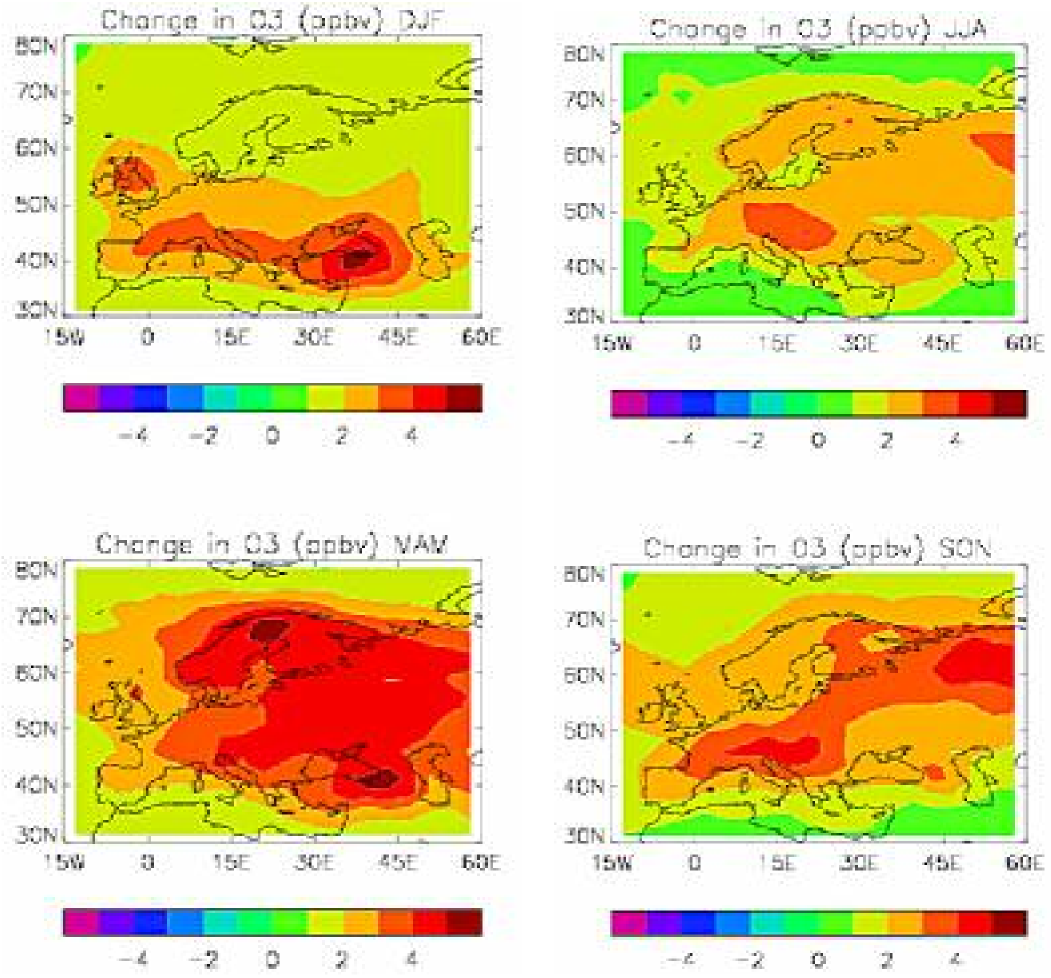

Figure 1. Changes in seasonal ozone due to exposing the plant stomata to doubled CO_2 concentrations.

The effect found above was purely due to the impact of CO_2 concentrations on the stomata. The climate was unchanged. The changed climate in a doubled CO_2 world would also be expected to affect the stomata through changes in heat and water stress. The meteorological changes are not only likely to be important in a seasonally averaged sense, but are likely to be particularly important during pollution episodes, and have yet to be quantified. Vautard *et al.* [2005] found that a simulation of ozone in the August 2003 European heatwave was improved by assuming a doubling of the surface resistance to ozone deposition.

The converse feedback whereby atmospheric composition and air quality affects climate can be strongly mediated by ecosystems. Sitch et al. [2007] showed that increased levels of surface ozone can damage plants sufficiently to reduce their carbon uptake. This translates to increased atmospheric CO_2 and a radiative forcing of up to 1.1 Wm^{-2} by 2100 due to anthopogenic emissions of ozone precursors since the preindustrial period.

Implications for modelling

The Met Office Hadley Centre is currently developing an Earth System model which integrates the climate, chemistry and ecosystem models. Figure 2 shows the structure of this model with many of the important couplings between climate, chemistry, aerosols and ecosystems.

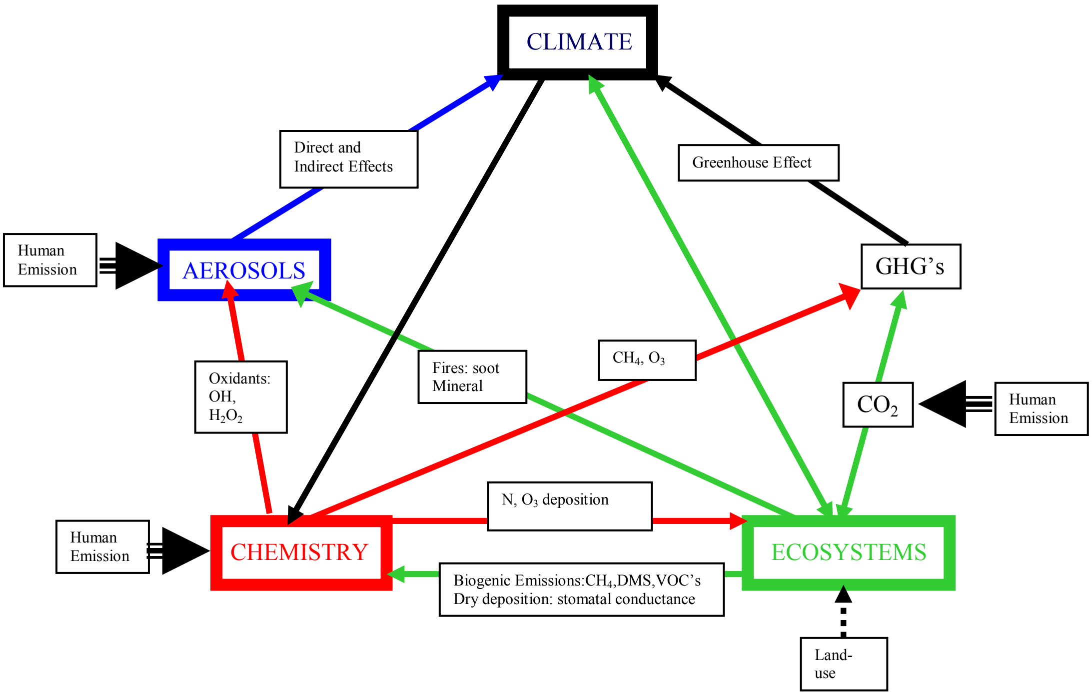

Figure 2. The Hadley centre earth system model (HadGEM) showing important coupling between the components.

The timescales for many of these interactions are sufficiently short that to be confident of incorporating them fully it is necessary to couple the processes within a GCM rather than in an offline manner. For instance the surface ozone concentration varies strongly throughout the day with the evolution of the nocturnal and daytime mixed layer, and with the levels of insolation. The opening and closure of plant stomata varies throughout the day too, in response to light levels, and stress levels. The ozone and stomata are intimately related in that, not only do the stomata affect the removal of ozone, but the damage caused by the ozone affects the stomatal opening. Hence this and other similar couplings within the earth system are best studied with an integrated earth system model in order to fully understand the relationship between air quality and climate.

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Modelling the Impacts of Climate Change on Air Pollution Levels in the 21st Century

A contribution to ACCENT CCAQ: Group 4

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Summary

A model system that is able to describe possible impacts of climate change on air pollution levels in the future has been established. The absolute dominating impacts from climate change on a large number of the chemical species are related to the predicted temperature increase. As a consequence of this temperature increase, the temperature dependent biogenic emission of isoprene is predicted to increase significantly over land by the DEHM-REGINA model. This leads to an increase in the ozone production which together with an increase in water vapour to an increase in the concentration of OH radicals. Furthermore this increase contributes to a significant change in the typical life time of many species, since OH are participating in a large number of chemical reactions.

Introduction

So far reduction of the anthropogenic emissions of chemical species to the atmosphere has been profoundly investigated. However, new research indicates that climate change also has a significant impact on the future air pollution levels. During the last couple of years, both global, hemispheric and regional modelling systems have been developed to describe the impacts of climate change on air pollution levels by different modelling groups all over the world. In the Department of Atmospheric Environment, National Environmental Research Institute (NERI) in Denmark, we have developed a hemispheric model system which shows good validation results. In the following section the model system will be described followed by some results and future outlooks.

Model systems

The DEHM model system (see Figure 1) consists of several combinations of re-analysis data and other meteorological input data to the DEHM model, which again can run in three different nested modes [Christensen, 1993, 1997 and Frohn *et al.*, 2002]. The resolution of the mother domain is 150 km × 150 km and it covers the majority of the Northern Hemisphere. The largest nest is covering Europe with a resolution of 50 km × 50 km and the smallest nest is covering northern Europe with a resolution of 16.7 km × 16.7 km. The DEHM model consists of a whole family of models including a POP-version, a CO_2-version, a full chemistry-version (called DEHM-REGINA) and others.

In the DEHM modelling system an option for modelling the impacts of climate change has been included by using meteorological input of the future provided by a climate model. The setup is described in Figure 2.

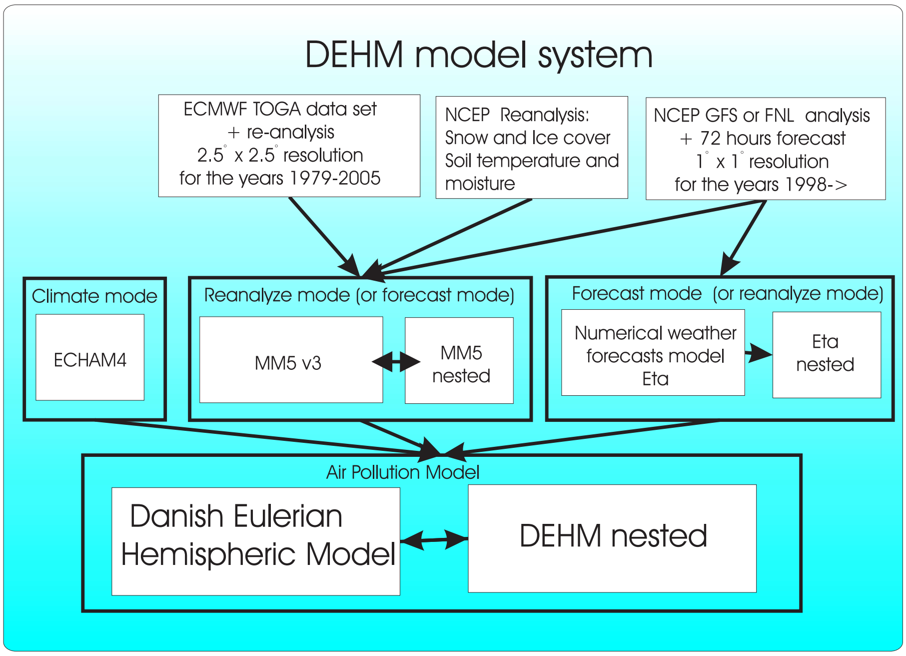

Figure 1. A schematic diagram of the DEHM model system.

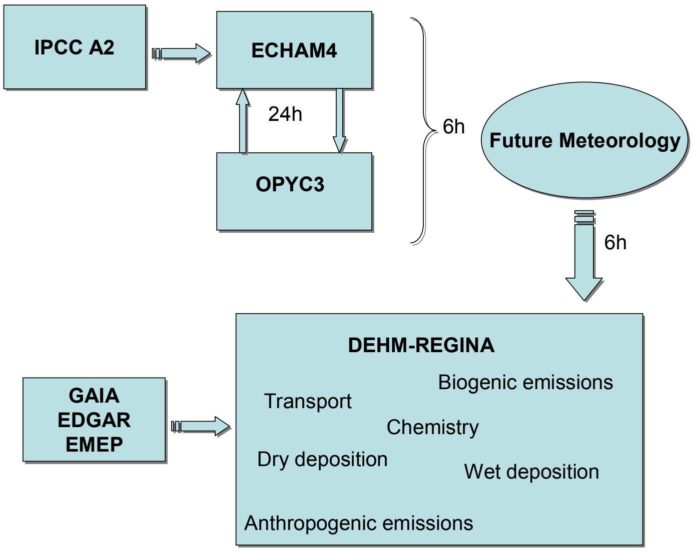

Figure 2. Off-line setup of the ECHAM4-OPYC3 and the DEHM-REGINA model. The climate simulation is forced with the IPCC A2 emission scenario. The output is saved every 6 hour and hereafter used as meteorological input to the chemical transport model DEHM-REGINA. Besides the meteorological input, DEHM-REGINA receives emission input from a combined data set (GEIA, EDGAR and EMEP).

As the name of the climate model ECHAM4-OPYC3 indicates, this general circulation model consists of an atmosphere (ECHAM4) and an ocean (OPYC3) component [Roeckner *et al.*, 1996, 1999]. The atmosphere model provides daily-averaged surface fluxes of momentum, heat and fresh water to the ocean model, which returns daily-averages of the sea surface temperatures, ice momentum and concentration as well as the ice and snow thickness. The output from the climate model is stored every six hours.

The six-hourly climate data is used as a one-way input to the DEHM-REGINA model (full chemistry version of the DEHM model). The DEHM-REGINA model also needs an emission input. The emissions of the primary pollutants consist of a combined set of data from the Global Emission Inventory Activity (GEIA) [Graedel *et al.*, 1993], the Emission Database for Global Atmospheric Research (EDGAR) [Olivier *et al.*,1996] and finally from the European Monitoring and Evaluation Programme (EMEP) [Vestreng, 2001] for Europe.

The chemical transport model DEHM-REGINA keeps track of the transport, chemistry, depositions and emissions of 63 chemical species and the model includes 120 of the most important chemical reactions between these species. Vertically the model is divided into 20 irregularly distributed layers extending from the surface of the Earth to the 100 hPa pressure level. The ECHAM4 has a different resolution and in order to use the meteorological fields as input data to the DEHM-REGINA model, a transformation of the meteorological data needs to be carried out before using it as input to the chemical transport model [Hedegaard, 2007]. So far no projections of the anthropogenic emissions of the entire 21st century exist and it is therefore not possible to study the absolute combined effect of climate change and human activities in the 21st century. Until now, several experiments have been carried out at NERI solely to study the effect from climate change on the air pollution levels in the future. The anthropogenic emission levels are kept at a constant level, which enables the DEHM-REGINA model to predict the changes in air pollution due to the impacts from climate change on the meteorology and biogenic emissions.

Results

The prediction of the air pollution of the 21st century is carried out as a time-slices experiment in order to save computing time. The three selected time periods are the 1990s, 2040s and the 2090s. The anthropogenic emissions are kept at a constant 1990 level in order to separate out the impacts from climate change. From a detailed analysis of many of the chemical species included in the DEHM-REGINA model it is concluded that the trend is very similar for the first 50 year period (1990-2040) and the second 50 year period (2040 to 2090). Therefore only the changes between the 1990s and 2090s are discussed in the following.

The temperature is increasing everywhere in the domain and it is by the ECHAM4-OPYC3 model predicted to increase 3 ˚C on a global average. However, locally in the Artic region a temperature increase of up to 11 ˚C is foreseen. This general temperature increase with local hot spots over southern Europe and the Arctic is similar to other model results [Stendel *et al*. 2002].

The difference in the ten-year average ozone concentration of the two decades is displayed in Figure 3 (left plot). A latitudinal dependence is evident in this figure. Ozone concentrations increase in the future and the increase gets stronger with increasing latitude. North of approximately 30 ºN the increase is highly significant (see right plot of Figure 3). South of 30 ºN the difference in ozone concentration changes and in the equatorial areas the ozone concentration levels tend to decrease significantly between the two decades. However, also a blurred land-ocean contrast in the ozone increase is evident and the ozone concentration generally increases less over the ocean.

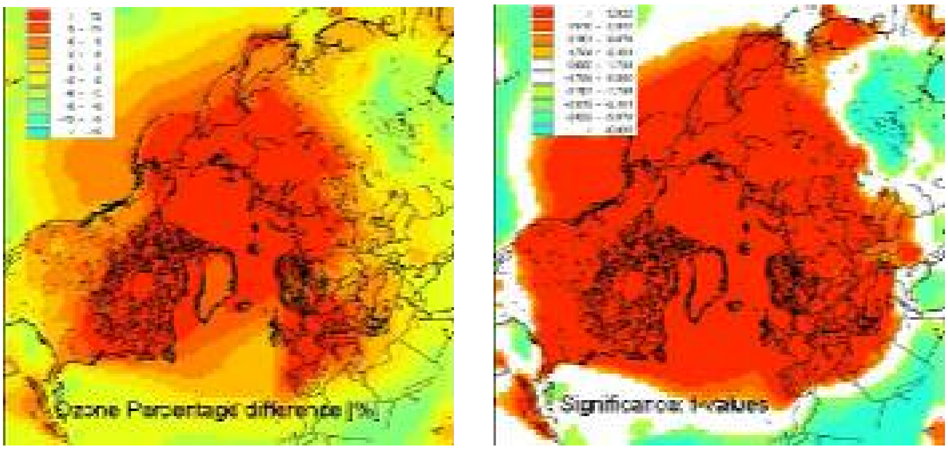

Figure 3. The difference in ozone concentration between the mean values of the two decades 2090s -1990s in percent. Right: The statistical significance of the changes of mean values between the two decades according to the t-test. The threshold value for significance is chosen to be within the 0.95 fractile corresponding to the 10 % significance level (which is the same as the 1,734 percentile value in the plot). Red colours indicate a significant increase and green colours indicate a significant decrease.

The ozone production in the troposphere is strongly dependent on the presence of the precursors NO_x and volatile organic compounds (VOCs). In the experiment analysed here, the anthropogenic emissions are kept constant. However, VOCs also have biogenic emitters, which can alter their emissions due to changes in the meteorological conditions. The only natural VOC emission included in the DEHM-REGINA model is the emission of isoprene. Isoprene is through participation in chemical reactions with OH, acting as a sink for OH radicals. Isoprene is also, through the role as ozone precursor, a source to the production of OH radicals. In DEHM-REGINA, the submodel BEIS (Biogenic Emissions Inventory System) is included to account for the biogenic isoprene emissions [Guenther *et al.* 1995]. Isoprene is emitted from trees and other plants and therefore primarily present over land.

The concentrations of isoprene are predicted to increase significantly where there are emitters present (not shown), for further details see Hedegaard, [2007] and Hedegaard *et al.*, [2007]. The general increase in isoprene concentration over land due to the temperature increase can contribute to explain the increase in ozone concentration, which posses a blurred land-sea contrast in the distribution field. The projected observed level of isoprene will alter the ozone production in a positive direction and thereby enhance the ozone level. These findings are in line with other studies [Tuovinen *et al.*, 2002, Langner *et al.*, 2004, Murazaki and Hess, 2006].

Furthermore an enhanced conversion rate is found in this changed climate. By the projected general increase in ozone and in specific humidity (not shown), it can be concluded that DEHM-REGINA predicts an increase in the reaction rates of a large number of chemical reactions over sea and at higher altitudes due to the resulting increase in hydroxyl radicals which will have a large influence on the life times of many chemical species. In Hedegaard [2007] it is shown that the life times of for example nitrogen dioxide will be reduced which leads to an increased level of nitrate and nitric acid. Also the sulphate production through the conversion of sulphur dioxide will increase in the future, for further details see Hedegaard, [2007] and Hedegaard *et al.*, [2007].

Impacts and importance in relevance to policy development

The coupling of the ECHAM4-OPYC3 climate model and the chemical DEHM-REGINA model is a very strong modelling tool with respect to studying impacts of climate change on air pollution. The model system has so far been established and shows fine evaluation results. A model system like this is very useful for both researchers and policymakers when assessment of the signal from climate change versus the signal from anthropogenic emissions is needed. The DEHM-REGINA model includes many chemical species which are relevant both in relation to human health and to nature. For example tropospheric ozone, nitrogen dioxide and particles impacts strongly on human health by affecting the respiratory system, which can lead to increased mortality. Persistent organic pollutants (POP) can affect the well-being of both humans and animals by reducing both the fertility and the ability to produce healthy progeny. Diseases like cancer and immune system failure can also be a result of increased POP pollution. Heavy metals on the other hand can affect the nervous and brain system of humans and animals. Both heavy metals and POPs have a tendency to accumulate within the food chain and therefore the strongest effects are found at the highest trophic level like for example human-beings.

Concerning the natural environment the DEHM-REGINA model can be used with respect to the assessment of both eutrofication and acidification of marine and terrestrial ecosystems. When emission threshold values are found for the agriculture and industry for the future decades, a climate-chemistry setup like the current can be very useful. So far only the effects of anthropogenic emissions have been accounted for when these threshold values have been established. However, the current results show that it is important also to account for the impacts of climate change alone in the future.

Future outlook

This study is only in the beginning of an accelerating research field with respect to the impacts of climate change on air pollution. The main conclusions from the experiment described here are that it is scientifically sound to run a chemical transport model on climate data and that the temperature increase predicted by a large number of climate models seems to have a dominating effect on the future air pollution levels and distributions [Hedegaard, 2007; Hedegaard *et al.,* 2007]. This study has created a wide range of new hypothesis, which will be very interesting to study and test in the future.

From the current results it has become evident that the biogenic emission has a very large impact on the future air pollution distribution due to climate change. Currently the parameterisation of the natural VOC emitters in the DEHM-REGINA model is only including isoprene. Terpenes are another group of VOCs, which are known to be released from biogenic sources as a function of temperature. The temperature dependent natural VOC emissions are composed of many contributions. Isoprene is known to produce ozone in contrast to terpenes, which are acting as a loss term for ozone, other parameters like the CO_2 level is also known to have an effect on the VOC emission. Therefore a sophistication of the biogenic emissions module in the model is one of the aims in the future.

Climate change affects air pollution. However, changes in air pollution levels of many species certainly also will affect the climate through for example contributing to the greenhouse effect or affecting the radiation balance in the atmosphere. So the ultimate aim in the future must be to establish a two-way coupled model system where feedback mechanisms between air pollution and climate can be represented.

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Building Multiscale Modelling Systems to Cope with the Interactions of Air Quality and Climate Change

A contribution to ACCENT CCAQ: Group 4

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Summary

This paper describes the current use of modelling tools for examining the links between climate change and air quality. The main reasons behind the uncertainties involved in the application of models and some suggestions for improving confidence in model predictions, particularly in the case of smaller scale applications, are also reported. Furthermore, some case study results dealing with air quality and climate interactions are presented to exhibit the state-of-the-art scientific understanding, while the main issues that require further research are also reviewed.

Introduction

In order to investigate the complex links between air quality and climate change, computer simulations are an indispensable tool. Confidence in the ability of models to describe climate and air quality is growing as the representation of many processes, such as the transport of water vapour and heat in the oceans as well as complex chemical transformations at smaller scales has significantly improved over the last decades. Climate models can currently provide credible simulations of climate, at least down to sub-continental scales and air quality models are increasingly successful in describing transport and transformation of gaseous and aerosol species at the regional scale. However, no model or model system is yet capable of satisfactorily simulating all important aspects of climate and air quality interactions, especially at the smaller scales.

Current use of modelling tools

General circulation models (GCMs)

The most detailed simulations of climate systems are currently produced by three-dimensional coupled atmosphere-ocean general circulation models. The physical equations governing the evolution of quantities such as temperature, moisture and momentum are solved and updated on timescales of typically 30 minutes. GCMs run at much coarser resolutions than weather forecasts models, typically of around 150 km, as the simulations have to cover extended periods, in some cases hundreds of years. The demand for long term runs also dictates that clouds, turbulence, convection and other small scale features are parameterised and not explicitly solved whereas the effect of Greenhouse Gases (GHGs) and aerosols is treated by a climate model radiation scheme. An additional important difference between CGMs and weather forecasting models is that the former need to include components of the climate system that are practically unchanging over the few days of a forecast, but change considerably over the period of hundreds of years that is characteristic for a climate change simulation. Thus, the most complex general circulation models also include equations representing the behaviour of the oceans, land vegetation and the cryosphere (sea ice, glaciers and ice caps).

Most models tend to be designed to simulate the chemistry of either the stratosphere or the troposphere. There are few attempts to simulate comprehensively the chemistry of both regions simultaneously. Reactive chemistry schemes have not yet been widely implemented in operational climate models. Instead, the concentrations of reactive, radiatively active gases such as CH_4, N_2O, O_3 and HCFCs, are usually fed into the models from databases generated by separate chemistry models. By failing to simulate the chemicals interactively, the models are not accounting for correlations between the chemical species and the meteorology in the model, but – perhaps more importantly – they do not allow for the changing climate to affect the chemical concentrations. The stratospheric chemistry models are an attempt to treat this problem, as they are used in a coupled mode, with the concentrations of the radiatively active gases interacting with the climate model's radiation scheme. Regarding aerosols, nearly all climate models include an interactive sulphur cycle. Other aerosol components are now being included in climate models such as anthropogenic black carbon and natural mineral dust. These aerosol schemes are necessarily highly simplified to reduce the computing time needed for typically long climate simulations. They thus lag a long way behind the sophisticated aerosol models used as research tools especially at smaller scales.

Regional climate models (RCMs)

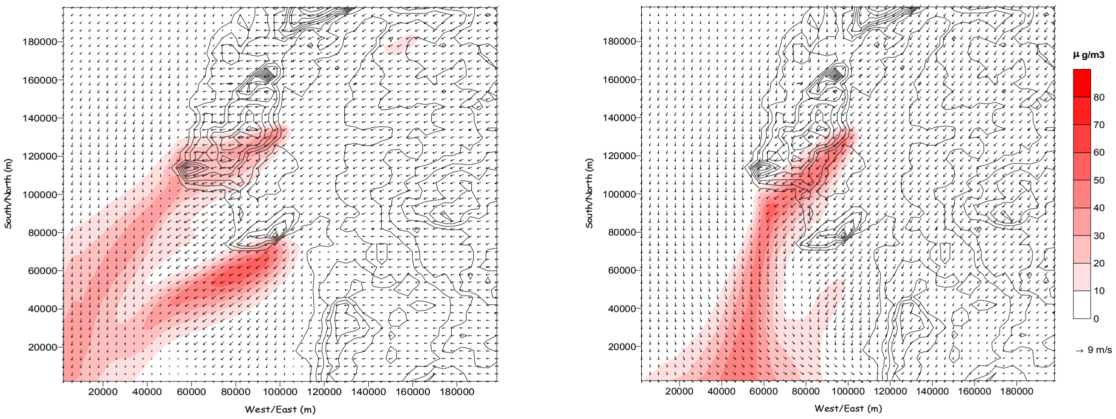
RCMs are used at higher resolutions than GCMs and thus allow for a more realistic representation of local topography and the effects of smaller scale features. RCMs can be embedded within the global model to provide information at higher resolution for a specific region, such as an area around an urban agglomeration of interest. As the predicted changes in surface temperature due to climate change will also depend on land surface type, a main advantage of the RCMs is the use of higher resolution land surface data. The use of RCMs is particularly recommended for realistically predicting local precipitation patters, as precipitation changes are very sensitive to small-scale orography features. RCMs are also appropriate when attempting to investigate the effect of regional air pollution, mainly aerosols, on regional climate.

Uncertainties related to RCMs may include a tendency to overestimate the variability of some small-scale processes, which may lead to the prediction of a higher frequency of extreme weather events than is realistic. This would in turn have implications for predictions of changes in frequencies of air pollution episodes. Moreover, RCMs may maintain and even amplify biases in the driving data from the global model. RCMs do therefore contribute significantly in improving the understanding of linkages between climate, atmospheric chemistry and global air quality as well as the assessment of future states of the atmosphere through its coupling with global-scale climate and chemistry models. However, the full details of their interaction with global as well as with local, smaller scale models, have not been worked out completely.

Chemistry transport models (CTMs)

In order to examine the full effects of atmospheric chemistry on climate and vice-versa, the application of CTMs seems to be an essential step. These perform calculations involving the transport and transformation of gaseous and aerosol species as well as their removal at the surface through deposition processes. The emphasis is on tropospheric chemistry while the chemical mechanisms used can exceed 100 species and several hundreds of reactions. In addition, emissions from natural sources such as vegetation or lightning are now calculated as fluxes interactively based on the changing properties of the vegetation or convective clouds, and interactive schemes are being added whereby the rate of deposition of chemical species on the surface depends on the changing vegetation and soil properties.

In the framework of an interactive air quality and climate change modelling system, CTMs can either be run online or offline. In online models, the chemistry code is run within the climate model. This is of particular importance for examining the links between air quality and climate change, as all the climate variables of the climate models are accessible to the chemistry model, while the radiatively active chemical species can also feedback on the climate. However, in the latter case, the difference in horizontal resolution between the chemistry and the climate modules needs to be addressed. An example case study where a regional CTM was coupled with a global system model, involved the development of a method to derive a computationally efficient urban air chemistry model from an urban airshed model. This “reduced form” urban air pollution model was then coupled to the MIT integrated global system model. This allowed for the global chemistry-climate model to provide more realistic and comprehensive predictions by taking into account urban air pollution [Mayer *et al.*, 2000]. In another interesting case study by Borrego *et al.* [2000], a GCM model, the NCAR Community Climate Model was combined with the MEMO/MARS mesoscale modelling system, consisting of the meteorological model MEMO [Moussiopoulos and Douros, 2003] and the photochemical model MARS [Moussiopoulos, 1995], in order to assess the impact of climate change (triggered by a doubled CO_2 concentration value) on regional ozone concentration and distribution. The study revealed important deviations in ozone spatial distribution between the two cases (Figure 1).



a. Control scenario

b. 2 × CO_2

Figure 1. Ozone concentration and wind fields for the Lisbon region, (a) at 12:00, for the control scenario and (b) the double CO_2 concentration scenario.

Scientific issues for further research

Chemistry

Atmospheric pollutants such as ozone and aerosols are either directly affected by climate processes through transformation, transport and deposition processes or indirectly through the impact of changing climate on their natural and/or anthropogenic emission rate and the abundance of their precursors. Ozone, in particular, is sensitive to changes in climate as the chemical reactions that lead to its formation in the troposphere are temperature and radiation dependent (Figure 2). Additionally, biogenic emissions of volatile organic compounds, a precursor to ozone, also rise with elevated temperatures. Higher temperatures as a result of climate change may thus increase the frequency and intensity of ozone episodes in future summers. A number of relevant modelling studies have been conducted having in mind the investigation of this correlation. For example, NASA-GISS global climate model at $4^o \times 5^o$ resolution was linked to the NCAR Mesoscale Model 5 and the CMAQ atmospheric chemistry model [Knowlton *et al.*, 2004]. The study provided valuable insight on the impact of climate change on regional air quality by simulating hourly regional meteorology and ozone in five summers of the 2050s decade across the New York metropolitan region.

Commonly overlooked factors linked with the impact of other pollutants is the transport of NO_x from urban areas to remote regions and contribution to the formation of secondary organic aerosols (SOA). From the modelling perspective, these factors should be associated with an adequate treatment of city and megacity plumes and a way to deal with secondary aerosol formation at all modelling scales. Of equal importance, the effect of non-CO_2 emissions on climate may prove to be crucial over smaller timescales and at the regional and local scales.

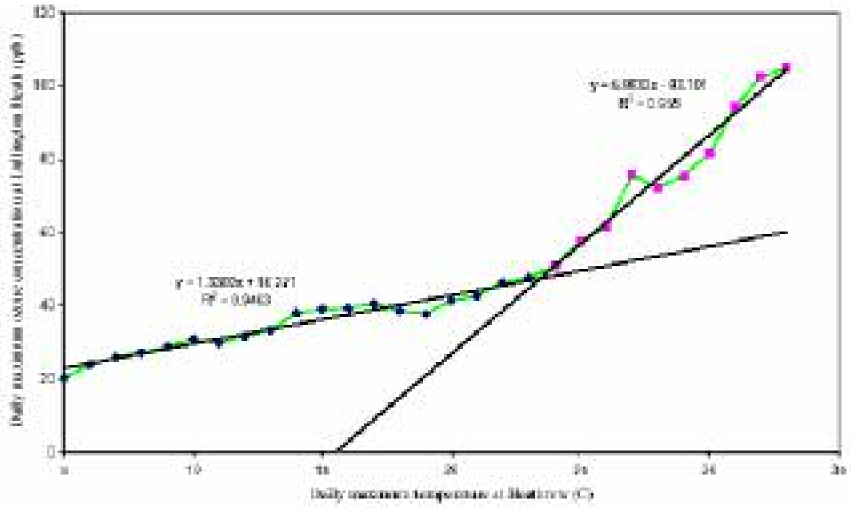


Figure 2. Relationship between daily maximum temperature at Heathrow and daily maximum ozone concentration at rural Lullington Heath, UK, 1993-1998 [Anderson *et al.*, 2001]

Meteorology

Basic understanding of the processes that control the atmospheric water vapour and clouds must be improved and incorporated into models of all scales down to the local scale. Some of these processes concern changes in the amount and spatial distribution of clouds as the water vapour in the atmosphere increases, and in the detrainment of moisture from clouds as a function of height.

On the other hand, predicting regional and global climate requires an understanding of the radiative effects of aerosol particles of natural and human origin, their cloud nucleating properties and their effects on precipitation, therefore attributing equal importance on the direct as well as their indirect effects. Some processes associated with indirect aerosol effects, as the increase in cloud lifetime suppression of precipitation due to larger number of smaller droplets formed in areas with high atmospheric aerosol load, the modification of high level ice clouds or the destruction of ozone and heterogeneous chemical reactions are fairly complex. Importantly, indirect aerosol effects are nonlinear with respect to the aerosol concentration. Therefore, small changes in the aerosol concentrations may lead to quite substantial radiative forcing. It must be underlined that estimates of total radiative forcing given above are model dependent and very uncertain. The impact of aerosol on the local scale radiative balance can be also large (up to 25 % or more) and equally complex. This forcing depends on aerosol concentration and composition and the aerosol mixing state [Hansen *et al.*, 2005]. Further evidence of local effects of aerosols on clouds are manifested for example in ship tracks or condensation trails from aircrafts, but more research, probably facilitating improved modelling techniques, is needed for understanding the global implications of these effects and the effects on precipitation and the hydrological cycle. Yet another type of interaction between aerosol concentrations and climate is related to the absorption of solar radiation by the aerosols, which can contribute to local warming of the atmosphere. An example of light absorbing particles is carbon soot generated from combustion processes or forest fires.

Towards investigating the two-way interaction of aerosol concentration and local climate change, one of the most obvious methodologies is the coupling between an appropriate chemistry model and a mesoscale meteorological model. For example, the mesoscale meteorological model MEMO and the 3-D dispersion model MARS-aero are currently being combined through a suitable interface. The aerosol module in MARS includes major organic and inorganic species which allows for an adequate description of the aerosol content in the lower troposphere. This is in turn fed into the meteorological model MEMO which simulates the mesoscale circulation based on a modified radiation budget as a result of the direct aerosol forcing. A set of simulations are currently being performed to investigate the capability of different parameterisations to describe aerosol-radiation interactions. On the basis of this analysis, parameterisations most appropriate for application in regional/global climate models could be identified.

Ambient concentrations of fine particles and other gaseous pollutants are controlled except for temperature, by several other meteorological variables, such as wind speed and precipitation patterns (Figure 3).

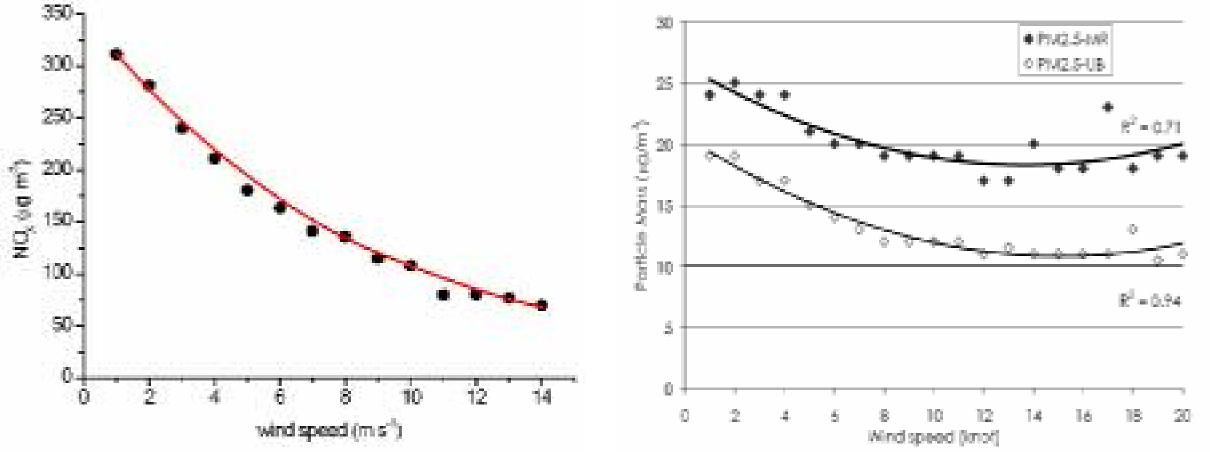


Figure 3. Wind speed versus concentration of nitrogen oxides at the London, Hillingdon automatic urban network station and particle concentration at Marylebone (MR) and Bloomsbury (UB) stations [DEFRA, 2007].

Emissions of aerosol particles including natural sources *e.g.* sea-salt and dust are presently poorly known and poorly represented inside models of all scales. In addition, some semi-volatile organics easily change phase as their phase-partitioning depends on temperature and dilution factors. It is thus important for aerosol particle emissions to be included in models as a process and not as a fixed number input from a database, as emission rates – including both mass and number of particles – depend largely on atmospheric conditions and must be known with good temporal and spatial accuracy.

Finally, the speed and timing of climate change strongly depends on how the oceans respond. The latest climate models are only just beginning to represent the processes which exchange energy between the atmosphere and ocean depths, so this remains an important source of uncertainty. This is also important as sea surface temperature (SST) is an important parameter affecting model results even at the regional and local scales.

Also, to date, there has been little effort to link climate change and land use/land cover models in assessments of potential future impacts of heat stress and air quality. Climate-ecosystem models are the necessary tools in order to investigate this link, from offline models which lack feedbacks, to their asynchronous coupling to global climate models, and finally to their synchronous and fully dynamic coupling to climate models.

The issue of scale interaction and model resolution

Implementing a multi-scale modelling approach that is able to incorporate the effect of the highly non-linear atmospheric chemistry of urban areas in global scale models is of vital importance. There is a considerable gap between the horizontal resolution of approximately 150 km of the climate models to the typical 10 km resolution of the models used at the regional scale. This means that important meteorological features such as frontal systems are poorly represented. Climate models try to represent processes they cannot resolve by parameterisations, which nevertheless are only approximate representations and should be tested against very high resolution large-eddy simulations or cloud-resolving models to quantify the effect of the approximation. In order to link climate predictions from a larger spatial scale to the regional level, an additional option to model coupling (using one-way or, preferably, two-way nesting) includes statistical down-scaling using the statistical relationship among local and larger-scale variables. Similar in concept to down-scaling, methods for up-scaling from regional scale models need to be further developed so that they will allow for the realistic simulation of transformation of emitted pollutants before they have been dispersed to the scale of the climate grid. These transformations include the coating of freshly-emitted soot by gas-phase material, organic aerosol transformations, and the general transition of particulate matter from a relatively hydrophobic state to one more hydrophilic [Hansson and O’Dowd, 2006]. The state at which the soot, in particular, ages to become hydrophilic is one of the key uncertainties in global predictions of aerosol radiative forcing and such up-scaling models have great potential to improve this aspect. Up-scaling is thus an issue for (a) emission inventories, (b) PM number and size distributions, and (c) aerosol ageing, specifically the hydrophobic to hydrophilic transition.

Another method is the use of surface-type data “tiling”. In tiling, the surface exchange scheme, which calculates the interaction between the surface and the atmosphere is run for each surface type (‘tile’) separately, and it is the net effect on the atmosphere that is averaged over the grid square, rather than the original surface types. This means that the model calculates a set of different surface temperatures for each surface type within the grid square and thus it is possible to distinguish the different expected climate change effects on surface temperature over urban areas from those over grassland or forests.

Conclusions

Although models are the most relevant scientific tools for examining the links between climate change and air quality, model predictions are subject to uncertainty and should ideally be complemented by satellite or *in situ* measurements. Uncertainties in model predictions arise from a wide variety of factors, including the quantification of certain input parameters such as emissions, as well as the sensitivity to physicochemical parameterisations. Dealing with the climate change and air quality interaction poses even greater challenges. The necessary interplay between the scales introduces additional technical difficulties while at the same time it remains a central aspect of the whole endeavour. A number of studies have recently verified the feasibility of coupled air quality and climate models, but a lot more steps need to be made towards reliable and efficient tools of this kind.

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A Network for Long-Term Measurements of Volatile Organic Compounds within WMO/GAW

A contribution to ACCENT CCAQ: Group 4

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The need for a VOC network in GAW

The WMO Global Atmosphere Watch (GAW) programme is designed to monitor and document changes in atmospheric composition over long time periods (decades). It has a globally distributed network of stations measuring a range of important compounds including ozone, carbon monoxide, carbon dioxide, methane, nitrous oxide and chlorofluorocarbons (and related molecules). A new initiative has now been proposed to create a global network of VOC measurements within GAW. This is the subject of GAW Report No. 171 which describes an expert workshop on global long-term measurements of volatile organic compounds (VOCs) held in Geneva early in 2006. The main purpose of making measurements of VOCs in a worldwide network is their use as tracers of atmospheric emission, transport, mixing, chemistry, particle formation, scavenging and deposition. This particularly includes identifying emissions from various source types (industrial, biomass burning, *etc*), probing long-range transport, and quantifying chemical processing by different types of radicals (hydroxyl, nitrate radical, halogens). Knowledge of their distribution, their variation with respect to time and their correlation with other species can provide unique information on the workings of the atmosphere. Furthermore, some VOCs are known to act as precursors to aerosols, both sulphate and carbonaceous, which can play a role in global change. In fact, lack of information on the distribution of these species introduces considerable uncertainty in climate models.

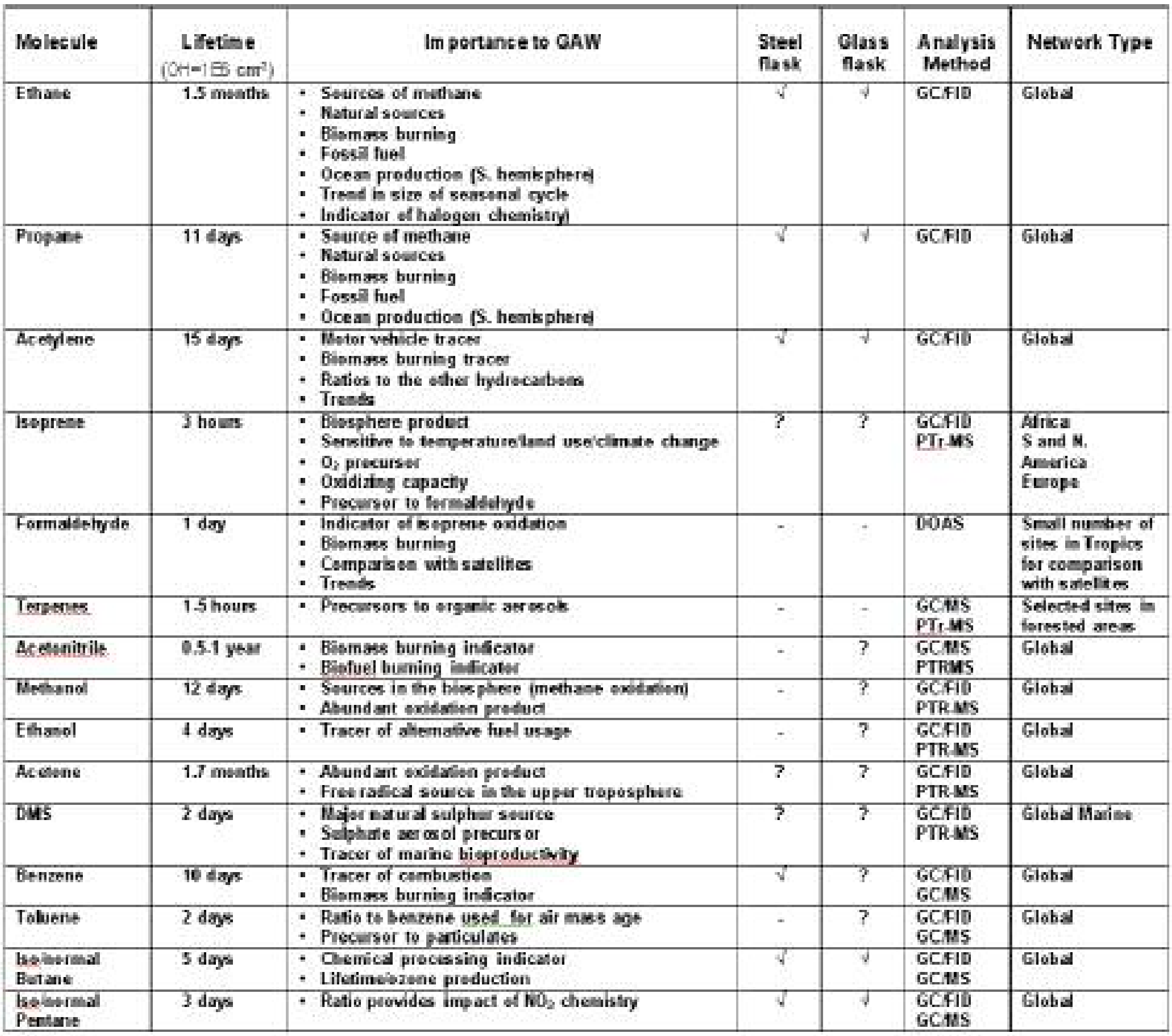
Consideration of VOCs for inclusion in the GAW programme

VOCs provide much information on atmospheric properties which can be used by modellers to validate their models. For GAW purposes it is not necessary to measure many VOCs since their concentrations at typical GAW stations will be too low for them to be measured using the standard technology. It is necessary to focus on compounds that are likely to be easily measurable in the more remote atmosphere, and that provide information about vital processes such as the sources of methane, the influence of biomass burning on atmospheric composition and, if possible, the efficiency of atmospheric oxidation. Table 1 is a summary of what is currently possible and why it is necessary. It lists target molecules with their lifetime with respect to hydroxyl radical chemistry, the reasons for their inclusion in the GAW database, their currently known stability properties in containers of different materials, and the extent of the measurement network which is feasible. The proposed compound list in Table 1 is projected to be realised as a programme within the GAW Strategic Plan Implementation period 2008-2014.

A global network of flask samples supported by intensive *in-situ* measurements

The Global Network is shown below. It consists of more remote stations where regular air samples will be collected in glass flasks to be analysed as part of the NOAA/INSTAAR-CU VOC programme based in Boulder Colorado. Further metal canister flask samples will be collected within the EMEP programme. The flask samples will be supported by much more frequent measurements at some sites where a more intensive programme of measurements will be conducted. Also many other trace species in the GAW programme will be measured simultaneously at these latter sites, such as ozone, carbon monoxide, carbon dioxide *et*c. The VOCs will then fulfil their role as tracers for sources of the more abundant species.

Table 1. VOCs for inclusion in the GAW Programme together with their significance and analytical considerations.

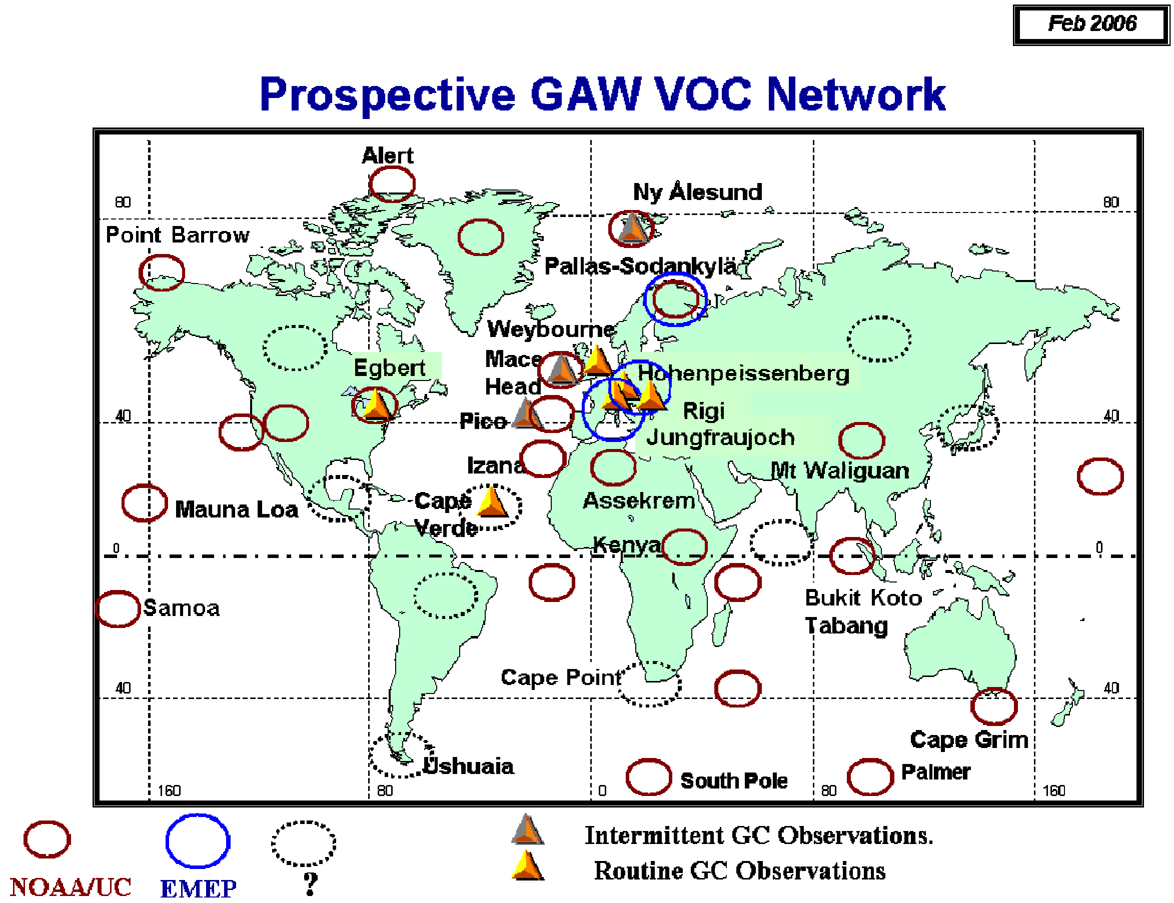


Molecule	Lifetime (OH=1E6 cm^{3})	Importance to GAW	Steel flask	Glass flask	Analysis Method	Network Type
Ethane	1.5 months	• Sources of methane • Natural sources • Biomass burning • Fossil fuel • Ocean production (S. hemisphere) • Trend in size of seasonal cycle • Indicator of halogen chemistry)	√	√	GC/FID	Global
Propane	11 days	• Source of methane • Natural sources • Biomass burning • Fossil fuel • Ocean production (S. hemisphere)	√	√	GC/FID	Global
Acetylene	15 days	• Motor vehicle tracer • Biomass burning tracer • Ratios to the other hydrocarbons • Trends	√	√	GC/FID	Global
Isoprene	3 hours	• Biosphere product • Sensitive to temperature/land use/climate change • O_3 precursor • Oxidizing capacity • Precursor to formaldehyde	?	?	GC/FID PTr-MS	Africa S and N. America Europe
Formaldehyde	1 day	• Indicator of isoprene oxidation • Biomass burning • Comparison with satellites • Trends	-	-	DOAS	Small number of sites in Tropics for comparison with satellites
Terpenes	1-5 hours	• Precursors to organic aerosols	-	-	GC/MS PTr-MS	Selected sites in forested areas
Acetonitrile	0.5-1 year	• Biomass burning indicator • Biofuel burning indicator	-	?	GC/MS PTRMS	Global
Methanol	12 days	• Sources in the biosphere (methane oxidation) • Abundant oxidation product	-	?	GC/FID PTR-MS	Global
Ethanol	4 days	• Tracer of alternative fuel usage	-	?	GC/FID PTR-MS	Global
Acetone	1.7 months	• Abundant oxidation product • Free radical source in the upper troposphere	?	?	GC/FID PTR-MS	Global
DMS	2 days	• Major natural sulphur source • Sulphate aerosol precursor • Tracer of marine bioproductivity	?	?	GC/FID PTR-MS	Global Marine
Benzene	10 days	• Tracer of combustion • Biomass burning indicator	√	?	GC/FID GC/MS	Global
Toluene	2 days	• Ratio to benzene used for air mass age • Precursor to particulates	-	?	GC/FID GC/MS	Global
Iso/normal Butane	5 days	• Chemical processing indicator • Lifetime/ozone production	√	√	GC/FID GC/MS	Global
Iso/normal Pentane	3 days	• Ratio provides impact of NO_2 chemistry	√	√	GC/FID GC/MS	Global

GC-FID is Gas Chromatography- Flame ionization detection. GC-MS is GC- Mass Spectrometry,

DOAS is Differential Optical Absorption Spectroscopy; TRMS is Proton Transfer Reaction Mass Spectrometry,

√ indicates state of current practice



The extensive global network will provide important information for the first time on latitudinal and longitudinal distribution of VOCs as well as their seasonal behaviour. This will be very valuable for testing global models of atmospheric chemistry and transport.

EMEP Monitoring Strategy beyond 2009

A contribution to ACCENT CCAQ: Group 4

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Summary

Long-term monitoring of atmospheric composition in combination with research oriented studies to provide information on atmospheric processes has been implemented as the basis for policy abatement for regional air pollution. This allows a description of spatial and temporal trends, and to validate and improve models. The EMEP monitoring strategy for the period 2004 to 2009 include several new approaches compared to the previous strategy. At present preparations are made for the next revision (to be concluded in 2009). It is expected that issues like synergies between different environmental topics (*e.g.* climate change, air quality and regional scale air pollution), extension of the geographical scope as well as new technologies like satellite remote sensing and data assimilation will important in the future strategy.

This presentation outlined the process for revision of the EMEP monitoring strategy for the consideration of the ACCENT community.

Introduction

The EMEP monitoring strategy 2004-2009 was adopted in 2004. It introduced an extended list of parameters to be measured and more formal requirements for its Parties. There was a specific focus on the geographical extension of monitoring. The strategy introduced a level approach for monitoring combining traditional monitoring sites with a limited number of *supersites.* The latter provided a strengthened involvement from national and European research efforts. At present, the full implementation is still pending, but several positive effects can be identified, including important discussions and increased awareness on the national level resulting in revised priorities, an improved relationship with AQFD monitoring requirements. For particulate matter, there are large improvements wrt aerosol supersites (EUSAAR) but for other compounds implementation is less encouraging (*e.g.* POPs monitoring). There is also a lack of monitoring capacities for oxidants and their precursors. The use of campaigns has been proven important, and also the increased interest of the scientific community has been a success.

EMEP monitoring in the years to come should address potential synergies wrt climate change needs. There is a large overlap in parameters of relevance as well as in the infrastructures established for monitoring. There is also great potential for additional future funding from the ECs FP7 Capacities programme. EMEP is in the process of becoming a member of GEO and will thus contribute to GEOSS. The EMEP database currently form a basis for the GEOMON one-stop shop for atmospheric composition. Also the combined use of data from multiple platforms (*in-situ*, satellite and ground remote sensing *etc*) is expected to be more pronounced in the future monitoring approaches. Data assimilation initiatives further request near-real-time data provision and EMEP will review its data reporting procedures to address also such issues.

The geographical coverage is still a challenge with relatively few sites in the east and south regions of the EMEP domain. The EMEP Task Force on Hemispheric Transport of Air Pollutants (www.HTAP.org) is currently conducting a modeling exercise to quantify intercontinental fluxes and will also provide input on monitoring needs. At the hemispheric scale, an even stronger link between climate change processes and regional air quality issues is evident. The application of “Export/Import sites” is essential. Also the link between regional pollution and local air quality issues will be central. At present, regional supersites are in place, but the ability to study processes on the urban scales are not well developed and coordinated, and data are generally only available from specific campaigns.

The EMEP monitoring in the years to come need to reflect the overall challenges which the CLRTAP is targeting. All current issues (Eutrophication, Particulate matter, Photooxidants, HMs/POPs and Acidification) will still be of relevance and a better understanding still needs to be developed. Contributions to other themes like climate change, biodiversity, biogeochemical cycles, hydrological cycle, land-use changes, biomass burning and others could offer additional use of the EMEP monitoring capcity.

The approach of the revision will be based on an adjustment rather than a major revision of the current strategy. It will be developed through the active involvement by the Task Force on Measurements and Modelling, the Task Force on Hemispheric Transport of Air Pollutants and the EMEP Steering Body. In the initial phase, there will be provided a review of the implementation of the current strategy for identification of gaps [2008]. Efforts will be made to ensure harmonization with other initiatives through consultations etc. The strategy is expected to be adopted by the Executive Body by December 2009.

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Towards an “Ensemble Model Observatory” for Air Quality Changes

A contribution to ACCENT CCAQ: Group 4

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Introduction

Air quality and the atmospheric composition near the ground undergoes and will undergo several changes in the future. The main driving factors of these changes are the evolution of the worldwide emissions, their regional characteristics, and the climate change forcing. Figure 1, taken from Vautard *et al.* [2007] shows, as an example, the evolution of some percentiles of the daily maxima over a homogeneous set over a few tens of European stations of the EMEP monitoring network. While the median does not undergo major changes the highest values decrease over Europe. The major heat wave of 2003 did not produce a 90th percentile higher than those of 1994 and 1990.

The extrapolation of the curves shown in Figure 1 is difficult to predict. It is not clear whether this downward trend will continue in the future, especially due to the additional increase of global baseline ozone due to global emission increase [Simmonds *et al.*, 2005]. Szopa *et al.* [2006] showed that over Europe the superimposition of these to drivers lead to a contrasted response. Not clear either is whether a situation like 2003 will become more frequent in the future as a result of the increase of extreme weather patterns due to climate change. Supposedly, a drier Europe will lead to more heat waves, an increase in summer stagnation and temperature extremes like in 2003 [Schär, 2004], and thus a climate-driven increase of ozone highest percentiles.

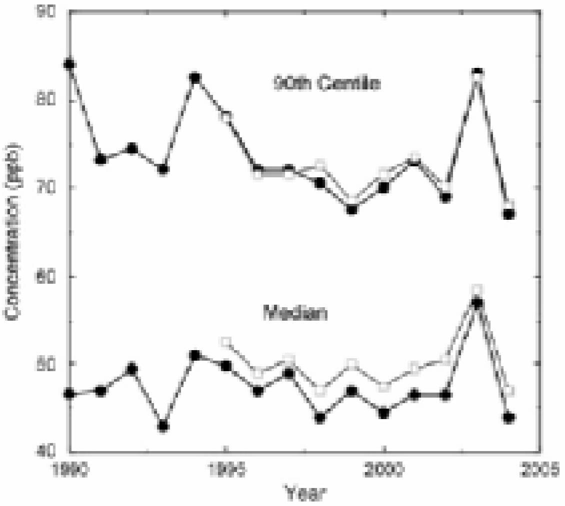

Figure 1. Median and 90th percentile of the ozone daily maxima (ppb) for each summer (JJA season), calculated over a set of 34 stations with homogeneous (no large missing periods or breaks) data from 1990 to 2004 (solid circles) and from another set (61 stations) with homogeneous data from 1995 to 2004 (open circles). After Vautard *et al.*, [2007].

Another possibility is that summer seasons follow one another with an increasing interannual variability in climate, alternating from extremely rainy to extremely warm and anticyclonic weather.

It has been suggested that recent summer extremes like the 2003 or 2006 heat waves in Europe provide prototypes of future summer air quality. These phenomena were studied intensively using models [Struzewska and Kaminski, 2007; Vautard *et al.*, 2005], and results showed in particular the large-scale nature of the ozone episodes.

Ensemble modelling of air quality changes

Air quality in recent climate extremes has been simulated only by individual groups and models, but no general and comprehensive view of the ability of models to simulate these extremes has been brought yet. However such an analysis is crucial in order to evaluate whether current air quality models are able to simulate and thus predict future air quality. One possibility would be to follow the Clean Air For Europe (CAFE) approach in simulating air quality changes under future emission policies using an ensemble of models [Cuvelier *et al.*, 2007; Van Loon *et al.*, 2007]. Figure 2, borrowed from Cuvelier *et al.* [2007], shows the spectrum of responses simulated by several models, to an array of emission control scenarios for 2010 for several European cities. As shown by the figure, for some cities and scenarios the sign of the ozone response is different from one model to another, while for other cities models agree.

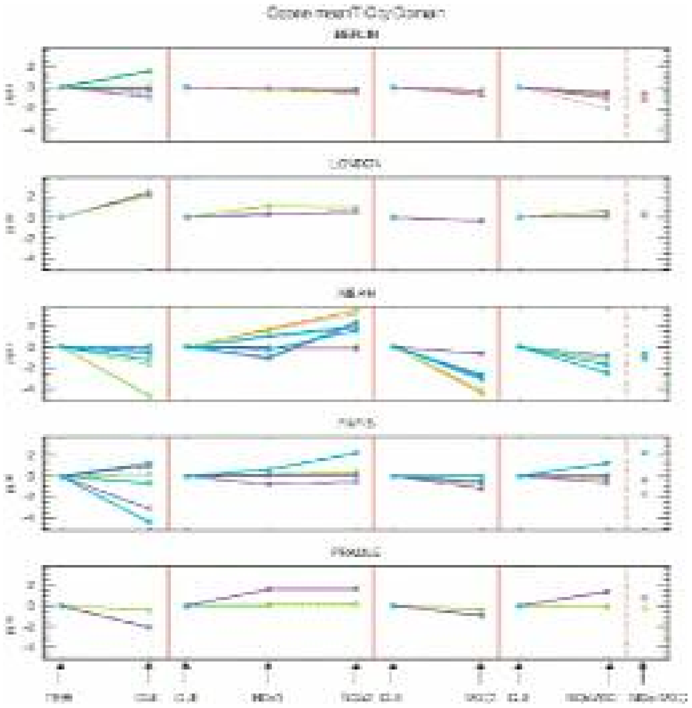

Figure 2. Comparison of mean ozone FS model responses to emission scenarios in the city domain. Each colour represents a given model as function of the emission scenarios specified on the abscissa axis. The last two points on the axis: NO_xVOC and NO_x+VOC identify scenarios with both NO_x and VOC reduced and the sum of NO_x and VOC reduced independently from each other. The vertical scale indicates the delta O_3 (ppb) between the 1999 base case and the considered scenario [Cuvelier *et al.* 2007].

As there are many uncertainties in air quality models, like biogenic emissions, deposition rates, boundary layer processes, *etc.* which are usually amplified by weather extremes, it is particularly interesting to assess the response of models, as an ensemble, in such conditions, and eventually predict the impact of climate change on air quality using the ensemble as in the City Delta project. As shown also in Vautard *et al.* [2006a], ensembles can also provide a quantitative prediction of uncertainty in air quality changes. Such a study can also be carried out for the extreme cases and for simulated future air quality.

Climate extremes impact on air quality are not the only phenomena calling for ensemble modelling. Decadal air quality trends have also been simulated independently using several models [Jonson *et al.*, 2005; Vautard *et al.*, 2006b], but no coordinated action was carried out using an ensemble for trends.

Conclusions

The coordination and development of an "air quality model observatory" made with an ensemble of models, for the assessment of air quality changes is probably essential to:

Evaluate model ability to simulate air quality in extreme weather

Evaluate model ability to simulate trends under emission control policies at regional or global scale

Evaluate model ability to simulate air quality trends

Evaluate model uncertainties in for such cases

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Air Quality and Climate Change – A Policy Perspective

A contribution to ACCENT CCAQ: Group 4

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Win-win policies and trade-offs

Policies to reduce atmospheric emissions of pollutants fall into two categories, those which also help to reduce emissions of air pollutants and greenhouse gases (GHGs) – the 'win/win' policies - and those where there may be antagonisms, either because GHG reductions lead to increases in air pollutant emissions, or *vice versa*. Examples of win-wins are measures which reduce energy use or polluting activities-energy efficiency measures, measures to reduce transport activity are obvious examples. Similarly the increased use of 'pure' or 'clean' renewables such as wind, wave or solar power with no polluting emissions of either type are win-win measures (assuming in the full life cycle there is a net reduction in emissions). Although there are many difficult issues surrounding nuclear power, in emission terms it is a clear win-win for air pollution and climate. In the transport sector, as well as measures to secure modal shifts to less polluting forms of transport, low carbon vehicles such as hybrids, electric and fuel cell powered vehicles should also benefit both air quality and GHG emissions. Several studies have shown that the co-benefits of win-win policies can be significant [Stern, 2007; EEA, 2006; Williams, 2006].

Some policies however can have opposite effects on air quality and GHG emissions. Many of these concern aerosol emissions and one of the largest effects is likely to be the reduction of sulphate aerosol, mostly from large industrial emitters such as power stations. On the one hand the reduction of sulphur emissions has been one of the great success stories in Europe and North America in the past three decades following the recognition of the acid rain problem and the successful reduction in acidic deposition during that period. It is however now recognised that sulfate aerosol exerts a cooling effect on the earth so reducing emissions of this pollutant in effect constitute an emission of a GHG. At the same time, the fitting of abatement technology such as flue-gas desulphurisation to power stations and large industrial emitters comes with a fuel penalty of the order of a 2-3 % of fuel consumption leading to a small increase in direct carbon dioxide emissions.

In the transport sector, the trade-offs between petrol and diesel vehicles provide another example. On the one hand diesel engines are inherently more fuel efficient than petrol ones but they also tend to emit more also emit more particles and NOx. In the UK in particular, the fraction of the car fleet which is diesel has increased significantly in the past decade, and may well continue in the future. A recent study [Mazzi and Dowlatabadi, 2007] showed that from 2001 to 2020 the additional mortality due to increased diesel use in the UK would be 1850 deaths (910 due to Euro 3 and 940 due to Euro 4). In a similar vein, an increase in biomass burning is on the face of it an extremely attractive way to reduce carbon emissions, and if the biomass is used in a mix with other fuels or with sufficiently stringent abatement equipment there should be minimal air quality impact. However, were large increases in biomass burning to take place in small combustion systems with poor combustion efficiencies and minimal abatement technology then the air quality impacts might be more significant.

Tropospheric ozone

One area where air quality and climate change concerns overlap is tropospheric ozone. There are several issues of importance here. Firstly, although emission control policies in Europe have successfully reduced short term peak ozone concentrations through controls on NO_x and VOC emissions over the past two decades, there is some suggestion that this downward trend is levelling off, and longer term projections [AQEG, 2006]suggest that summer photochemical episodes may become more frequent and intense as the climate warms. Moreover the contribution from biogenic emissions is also projected to increase, and this poses the policy maker with an additional problem, not least because emissions of biogenic VOCs are subject to large uncertainties.

Tropospheric baseline concentrations of ozone and their future trends are also of importance. The current baseline level is close to levels which are known to damage plants and vegetation so global increases in the baseline would clearly be of concern. Similarly, in urban areas in Europe, mean ozone levels are steadily increasing as NO_x controls on motor vehicles take effect, so that annual average ozone levels in urban areas are approaching the rural background level, which in turn is influenced strongly by the tropospheric baseline. This behaviour is potentially important for human health if there is reason to believe that there is no threshold for adverse effects from ozone, or if the threshold is lower than previously thought. This issue is currently the subject of intensive research in the health effects community.

Quantifying the trade-offs for policy

The issue of the conflicts between diesel and petrol car use has already been mentioned. There is a further feature to this problem involving the fitting of particulate filters to diesel vehicles as these currently result in a small fuel consumption penalty. A currently topical example is the public consultation recently carried out by the European Commission on possible emission limits for new heavy-duty vehicles. We therefore have not only the trade-off between the reduced black carbon/particulate emissions resulting from the addition of the filter, which have both health and climate benefits, but also the small increase in carbon emissions from the additional fuel consumption, which offsets to some extent the fuel benefit of the diesel vehicle. In quantifying these trade-offs one is therefore faced with trying to compare quantitatively the climate effect of a reduction in black carbon emissions with an increase in CO_2. This is by no means easy as the large differences in atmospheric lifetimes mean that the normal comparison via Global Warming Potentials is not valid. The problem has recently been addressed [Boucher and Reddy, 2007] using the concept of Global Temperature Potential [Shine, 2005]. The authors define a parameter:

$$\mathrm{X} = \mathrm{GWP}_{\mathrm{BC}}(T = 100\mathrm{years})\Delta \mathrm{x}_{\mathrm{BC}}/\Delta \mathrm{x}_{\mathrm{CO2}},$$

where Δx is the mass emission change, and derive limiting values which allow assessments to be made of whether or not there is an overall climate benefit for various time horizons. They further show how this concept can be generalised to compare the climate effects of carbon dioxide against a set of short-lived species. This represents a great advance in tackling the problem of comparing the climate effects of short and long lived species, an area where an international consensus is clearly needed.

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Transport and Transformation of Pollutants (T&TP) Access to Emission Data, Access to Laboratory Data, Aerosols, Remote Sensing from Space (AT2), BIAFLUX, Modelling

14 Appendices

A CCAQ Participants

Impact of Climate Change on Air Quality
4th ACCENT Barnsdale Expert Workshop

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Colin O'Dowd	NUI, Galway, IRL	colin.odowd@cmas.demon.co.uk	
Joe Prospero	Univ. Miami, USA	jprospero@rsmas.miami.edu	
Yinon Rudich	Weizmann Institute, Israel	yinon.rudich@weizmann.ac.il	

Group 4		**Modelling and observation tools**	
Peter Builtjes	TNO, Apeldoorn, NL	p.j.h.builtjes@mep.tno.nl	**Chair**
Oystein Hov	Meteo- Institute, Oslo, N	Oystein.Hov@met.no	**Speaker**
Laurence Rouil	INERIS, Paris, F	rouil@ineris.fr	**Rapporteur**
Steffen Beirle	MPI, Mainz, D	beirle@mpch-mainz.mpg.de	
John Burrows	IUP Bremen, D	john.burrows@iup.physik.uni-bremen.de	
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Martin Williams	Defra, London, UK	martin.williams@defra.gsi.gov.uk	

Organisation		
Peter Borrell	P&PMB Consultants, UK	pborrell@luna.co.uk
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Peter Borrell
P&PMB Consultants
Newcastle-under-Lyme, November 2007

B. CCAQ Programme

Impact of Climate Change on Air Quality
The 4th ACCENT Barnsdale Expert Workshop

Programme

Meetings and breaks are held in the Edith Weston Suite.
Meals are in the Spa and Restaurant Complex

Monday, 5th November 2007		
11.45 to 12.30	*Check-in (Hotel Reception)* *Registration (Edith Weston Common Room)*	
12.30	*Lunch (Osprey room)*	
13.30 to 14.00	*Registration (Edith Weston Common Room)*	
14.00	*Opening (Langham Room)* ***Chair*****:**	***Claire Granier***
	Welcome: the aims and organisation of the meeting	Paul Monks
14.15	News from ACCENT	Sandro Fuzzi
14.30	Impact on photo-oxidants, precursors and feedback mechanisms *Topic 1 plenary*	Solena Turquety
15.05	Formulation of Topic 1 issues	Ally Lewis
15.25	Impact on surface-atmosphere interactions *Topic 2 plenary*	Bill Collins
16.00	Formulation of Topic 2 issues	David Fowler
16.20	*Tea (Edith Weston Common Room)*	
	Chair:	***Colin O'Dowd***
16.50	Impact on aerosols and their precursors *Topic 3 plenary*	Thorsten Hoffmann
17.25	Formulation of Topic 3 issues	Johann Feichter
17.45	Building observation and modelling systems *Topic 4 plenary*	Øystein Hov
18.20	Formulation of Topic 4 issues	Peter Builtjes
18.40	Close	
from 19.00	*Mixer (Rutland room)*	
19.30	*Dinner (Osprey room)*	

Tuesday, 6th November 2007		
9.00	Group Discussions, Session 1 Discussion rooms: Group 1. *Rockingham* Group 2. *Hambleton* Group 3. *Whitwell* Group 4. *Langham*	
10.45	*Coffee (Edith Weston Common room)*	
11.15	Group Discussions, Session 2	
13.00	*Lunch (Osprey room)*	
14.30	Group Discussions, Session 3	
16.00	*Tea (Edith Weston Common room)*	
16.30	Group Discussions, Session 4	
18.30	Close	
from 18.45	*Mixer (Rutland room)*	
19.30	*Dinner (Osprey room)*	
Wednesday. 7th November 2007		
	Plenary *(Langham Room)* ***Chair:***	***Tony Cox***
09.00	Impact on photo-oxidants, precursors and feedback mechanisms *Topic 1 report*	***Stefan Riemann***
09.20	General discussion on Topic 1	Stefan Riemann and Ally Lewis
09.40	Impact on surface-atmosphere interactions; *Topic 2 report*	Chris Fletchard
10.00	General discussion on Topic 2	Chris Fletchard and David Fowler
10.20	Impact on aerosols and their precursors *Topic 3 report*	Hugh Coe
10.40	General discussion on Topic 3	Hugh Coe and Johann Feichter
11.00	*Coffee (Edith Weston Common room)*	
	Chair:	***John Burrows***
11.30	Building observation and modelling systems; *Topic 4 report*	Lawrence Rouil
11.50	General discussion on Topic 4	Lawrence Rouil and Peter Builtjes
12.10	What have we learned and where do go from here?	Paul Monks
12.45	*Lunch (Osprey room)*	
13.30	*Close*	

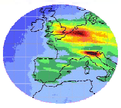
Peter Borrell
P&PMB Consultants, Newcastle-under-Lyme, October 2007

C. CCAQ Briefing Sheet

Transport and Transformation of Pollutants (T&TP)
Access to Emission Data, Access to Laboratory Data, Aerosols,
Remote Sensing from Space (AT2), BIAFLUX, Modelling

Impact of Climate Change on Air Quality

The 4th ACCENT Barnsdale Expert Workshop



AT2

Briefing Sheet

BIAFLUX

1. Meeting Arrangements

Aims of the workshop

a. To identify and review the key uncertainties in ascertaining the likely effects that the changing climate will have on air quality, on regional, local and urban scales.

b. To provide a basis for future collaborative research priorities in this area.

Discussion topics

The meeting will be organised around guided discussions on four topics:

Topic 1	Investigating changes in photo-oxidants, precursors and feedback mechanisms, with changing temperature and land use
Topic 2	Investigating changes in surface-atmosphere interactions with changing temperature and land use
Topic 3	Investigating changes in aerosols and their precursors with changing temperature, humidity and land use.
Topic 4	Building observation and modelling systems to cope with the interactions of air quality and climate change

Notes on the Discussion Topics

- Each topic should consider the effects of changes in emissions, due to changes in temperature, meteorology and land use.
- While emphasis will be on investigations of potential future changes, topics may include a consideration of the previous hundred years or so.
- The main issues should be emphasised, within the framework of the Strategy on Air Pollution and the new exceedance limits to be imposed.
- Topics should include large scale modelling, simulating changing meteorological fields, as well as detailed modelling and experimental process studies.
- If possible, some attention should be given to how to assess the controls and feedbacks in natural and anthropogenic emissions

Organisation of the Discussion

The meeting will start with a plenary session with invited review papers on each topic. Each will be followed by a short response by the Chairs of each group who will formulate the questions to be discussed. The groups will then separate. The final combined session will be devoted to reports from the Rapporteurs of each of the Groups and a general discussion on future directions.

Contributions to the discussion and written contributions

All invited participants are expected:

a. to contribute to the discussions with "voxboxes", *i.e.* one or more brief contributions of key points, results or conclusions, illustrated with one or two overheads; and

b. to produce *at or before the meeting* a brief one or two page extended illustrated abstract of their contributions, in a prescribed format, for publication in the meeting report, which will be produced in the series of ACCENT Reports.

Outcome of the Workshop

A report will be published by ACCENT indicating clearly the steps required to achieve solutions to the scientific problems.

Group Chairs, Rapporteurs and Speakers

	Chair	*Rapporteur*	*Speaker*
Group 1	Ally Lewis	Stefan Riemann	Solena Turquety
Group 2	David Fowler	Chris Fletchard	Stephen Sitch
Group 3	Johann Feichter	Hugh Coe	Thorsten Hoffmann
Group 4	Peter Builtjes	Lawrence Rouil	Øystein Hov

2. Roles of Speakers, Chairs, Rapporteurs and Participants

Role of the Participants

- The principal role is to participate! *i.e.* to contribute to the discussion on the various questions.
- Contributions to the discussion should be made as voxboxes – five minute verbal contributions supported by one or two overheads, which are pertinent to the question being discussed.
- Participants are welcome, at the discretion of the Chair, to make several voxbox contributions.
- *Prior to or at the meeting*, particpants should provide an electronic written version of their contribution/s, illustrated, if possible, with one or two figures. A contribution template can be downloaded from ftp://ftp.keele.ac.uk/pub/cha12/T&TP/CCAQ/CCAQ_Contribution_template.pdf

Role of the Plenary Speakers

- *Prior to the meeting*, speakers might wish to consult the Chair and Rapporteur for their topic on the questions and issues that require attention in the discussions.
- Speakers are invited to give a comprehensive overview of their respective topic.
- Within their talk, speakers should identify a number of current issues and questions that can serve as a basis for the subsequent discussions.
- The question session at the end of the lecture should concentrate on clarifying the questions which the discussion group should address.

- Recognising that a comprehensive discussion is to follow, it would be sensible if speakers refrained from providing definitive answers to the questions they pose!!
- *At or before the meeting*, speakers should provide an illustrated written account of their talk, which should include a list of questions and issues. This will be published in the proceedings. A contribution template can be downloaded from

  ftp://ftp.keele.ac.uk/pub/cha12/T&TP/CCAQ/CCAQ_Contribution_template.pdf

Role of the Chairs

- *Prior to the meeting*, Chairs might like to consult with the Plenary Speaker and Rapporteur for their topic on the questions and issues that require attention in the discussions.
- *Prior to the meeting*, you might like to contact some members of your group to raise particular issues.
- In the group discussions, Chairs should endeavour to see that all the questions posed are addressed.
- For each question, the Chair should endeavour to ensure that a clear statement emerges which can be recorded by the rapporteur and can be brought together with information from the other sessions to provide a definitive conference statement on the issue.
- Prior to the topic presentation, the Chair should assist the Rapporteur for their topic, in putting together the results of the discussion on the topic, for presentation and subsequent publication.

Role of the Rapporteurs

- *Prior to the meeting*, rapporteurs might like to consult with the Plenary Speaker and Chair for their topic on the questions and issues that require attention in the discussions.
- *In each of the group discussions*, the rapporteur should record the highlights of the presentations and the main points of the discussion, concentrating on providing clear statements which include the answers to and suggestions for tackling the questions and issues raised by the plenary speakers and Chairs. Specific recommendations for necessary work should be incorporated if possible.
- For the *final topic presentation*, the rapporteur should put together the conclusions of the group to provide a clear presentation on the issues and recommendations. The aim of the final discussion after the topic presentation is to consider and clarify the specific recommendations for future work and activities, and allow some interactivity between groups.
- The *final account for publication* should include the results, if any, of the final discussion.
  It would be helpful if the account contained one or more figures to illustrate the highlights
  of the discussion. A contribution template can be downloaded from
  ftp://ftp.keele.ac.uk/pub/cha12/T&TP/CCAQ/CCAQ_Contribution_template.pdf
- It would be appreciated if the rapporteurs could work up their final version and send it to *Peter Borrell* before the *30th November 2007.*

Peter Borrell
P&PMB Consultants, Newcastle-under-Lyme
October 2007

D. Barnsdale Pictures

photo: Oksana Tarasova

photo: David Fowler

Further pictures can be viewed on
http://www.worldhq.com/pborrell/family/events/events_2007_CCAQ/CCAQ_2007.htm