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

Volatile Organic Compounds in the Polluted Atmosphere

The 3rd ACCENT Barnsdale Expert Meeting

John Burrows, Tony Cox, David Fowler,
Claire Granier, Ivar Isaaksen, Paul Monks,
Colin O'Dowd and Peter Borrell
Editors

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Volatile Organic Compounds in the Polluted Atmosphere

The 3rd ACCENT Barnsdale Expert Meeting

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Volatile Organic Compounds in the Polluted Atmosphere

The 3rd ACCENT Barnsdale Expert Meeting

1. Executive Summary

Volatile organic compounds (VOC) play a central role in air pollution; they react with nitrogen oxides in the presence of sunlight to generate ozone and other photo-oxidants; they also, in the course of their various reactions, can form higher molecular weight organic compounds which condense to produce "secondary" organic aerosol (SOA).

While their general role in tropospheric chemistry is appreciated, the number of VOC and the complexity of the reactions which chemically degrade and oxidise them, means that there are many large uncertainties associated with VOC. These uncertainties feed into the chemical transport models used to describe the tropospheric environment, and so reduce their reliability in understanding, forecasting and assessing the troposphere.

SOA is formed from the less volatile products of the oxidation of VOC. These may condense on aerosol nuclei forming aerosol particles, and the compounds are partitioned between the gas phase and the liquid/solid phase on the particle. The importance of SOA has grown in recent years with the realisation that they may have effects on human health. By their very nature, the detailed chemical composition of SOA is seldom known and the aerosol is very difficult to characterise and quantify.

The 3rd ACCENT expert workshop was initiated to try to address some of the many uncertainties with respect to VOC and SOA, and to indicate research paths, by which the uncertainties could be reduced. The workshop was held under the auspices of seven ACCENT groups: Transport and Transformation of Pollutants (T&TP), Remote Sensing from Space (AT2), Access to Emissions; Access to Laboratory Data, Aerosols, BIAFLUX and Modelling.

The meeting was held at the Barnsdale Hall Hotel in Rutland on Monday, Tuesday and Wednesday 30th, 31st October and the 1st November 2007; some forty nine experts attended (*Appendix A*). The meeting was organised around three discussion groups, addressing the major areas of concern. There was a mixture of plenary talks and discussion sessions (*Appendix B*). All the speakers, chairs, rapporteurs and participants received detailed instructions to try to ensure that the discussions were as productive as possible (*Appendix* C).

The following conclusions and recommendations emerged from the three discussion groups. These were seen and commented upon by the workshop as a whole.

1.1. Emissions of VOC

General conclusions

Uncertainties in VOC emissions

The huge uncertainties in VOC emissions, particularly biogenic VOC and OVOC (oxygenated VOC), need to be addressed and current accuracy and precision of emission inventories need to be drastically improved.

Characterisation of VOC emissions

Adequate characterization of VOC emission variability (diurnal, weekend, seasonal, *etc.*) was identified as being crucial to our understanding of current and future emissions. New and existing platforms are required to make high quality long-term measurements with their scope based on science (rather than policy-based) criteria.

Analytical techniques

New analytical techniques need to be developed, refined, and widely deployed to measure concentrations and fluxes of VOC, especially OVOC, long-chain VOC, and reactive BVOC (biogenic VOC).

Submission of valid data

Data discipline on the part of scientists needs to be encouraged and better access to VOC emissions data needs to be facilitated.

Impact of global change

Predicting the effects of global climate change factors (such as increases in ambient CO_2, O_3, ambient temperature and response to droughts and flooding) on BVOC emissions is highly uncertain and requires an improved understanding of the biochemistry and physiology of emissions, including updating "Guenther's algorithm". This should be an extremely high priority for future investigation.

Specific recommendations for improving emission estimates for VOC

Priorities for anthropogenic VOC and OVOC

* Characterise the sources, fluxes and variability (diurnal, weekend, seasonal, climate, *etc.*) of VOC, especially OVOC and long chain compounds. The seasonal variation of solvent evaporative emissions, in particular, needs to be better characterized.

* Continue to develop, refine and widely deploy new analytical techniques for measuring concentrations and fluxes of VOC, especially OVOC.

* Make measurements to compare as many different cities as possible, to establish city "ecotypes", especially for cities in poorly-studied regions.

* Employ isotope studies to distinguish between anthropogenic and biogenic VOC sources, especially for OVOC.

Priorities for biogenic VOC

* The huge uncertainties in VOC emissions need to continue to be addressed. Current emission inventories need to be drastically improved.

* Many more compounds need to be considered and there is a need to include all major plant species.

* Primary emission measurements at branch or leaf level are needed, under conditions where fast oxidation reactions of released reactive VOC species are excluded.

Biogenic VOC responses to climate change

* Long-term year-round VOC flux measurements are needed, especially for tropical ecosystems for the better understanding of current emissions, and to monitor future changes.

* Light and temperature alone are not sufficient to predict the response of emissions to global change. There is a need to include seasonality, ecophysiology, water availability, *etc.* Circadian controls may also be important for how plants react to change.

Improving VOC within models

* Better speciation of AVOC by compound and emission category is needed, and a wider range of OVOC species need to be considered. Algorithms should be included for BVOC.

* Emission measurements are needed where there are large data gaps – *e.g.* tropical forest, Africa, South America. Funding will be required.

* There is a need to support primary emission measurements at a plant species level.

* Quality-controlled measurement data should be made available and submitted at the time of publication. Such data need to be submitted to a recognised archive in standard format to be widely accessible for use in models.

* Journals should be encouraged to mandate that references to data files, secured in a recognised archive, accompany any articles that are published.

* There is a need to secure long term resources to maintain a living, expert-validated emission inventory.

* Methodology for model comparisons requires better overlap of species in model emission inventories.

Recommendations for future satellite work

* Continue gathering data and adding measurement capability, for both satellite and terrestrial platforms.

* There is a need for higher spatial and temporal resolution satellite measurements.

* Geostationary satellite instruments are needed to capture and account for large diurnal trends in many measured compounds.

* More emphasis should be made on limb measurements because of their better vertical resolution.

* Improvements are needed in the knowledge of basic laboratory spectroscopy to underpin the spectroscopic determination of VOC.

QA/QC recommendations

* All VOC measurements reported to archives should be accompanied by appropriate supporting sampling protocol information.

* Good QA/QC protocols, for both AVOC and BVOC, need to be supported, including inter-comparisons where possible.

* There is a need to encourage the development of new technology to improve techniques to make and facilitate the sharing of standards.

Long-term measurements

* Existing long term measurement platforms should continue to be supported; the scope of VOC measured should be extended, and new, carefully selected, measurement sites in strategic remote, rural and urban locations added. New measurement techniques should be included as they become available.

* Satellite measurements should be developed and used to extend the scale of measurement stations.

* Priority species should be defined, including satellite products and global change compounds. One could build on recommendations for specific gases to measure from the recent WMO/GAW workshop. Glyoxal and supporting tracers such as

CO, methyl bromide and other halogenated VOC should be added to the list where possible.

* New modelling tools, such as particle dispersion models, should be further developed and employed to interpret measurement data in terms of changing emissions. Back trajectories, by themselves, are insufficient.

1.2. Uncertainties in local, regional and global processing of VOC

General recommendations

VOC and SOA: similarity in origin and treatment

The group recognised that, in trying to understand the atmospheric degradation of VOC, it is unrealistic to separate chemical processes generating oxidants (*e.g.* ozone, nitrates) from those which lead to the formation of SOA, since both are products of the same chemical processes.

Simplification of mechanisms

It was also recognised that the representation of such processes in the majority of atmospheric models needs to be substantially simplified. However it is essential to establish a sound methodology which allows fundamental information from laboratory and theoretical studies of elementary reactions to feed through to appropriate reduced mechanisms.

Availability of VOC kinetic information

Kinetic and mechanistic information related to the atmospheric oxidation of VOC are continuously being produced. Although some of the most important kinetic data are recorded in evaluated databases (*e.g.* IUPAC sub-committee on gas kinetics), the reactions of many VOC are not included at all. The group recommended that a new community-wide approach is required to produce a comprehensive current database of all relevant kinetic and mechanistic information. This needs to be coordinated on an international level and may require the assistance of publishers, as in other scientific areas, to ensure that reported data are inserted into a database at the time of publication.

Principal uncertainties

* The variation in VOC oxidation product distributions as a function of temperature and also at low NOx concentrations

* Kinetics and mechanisms for the reactions of NO_3 with multifunctional unsaturated hydrocarbons and large biogenic compounds.

* Mechanistic information for key anthropogenic compounds (aromatics and alkanes > C_5).

* Kinetics and mechanisms for the atmospheric degradation of nitrates, hydroperoxides and multifunctional organics.

* The reactivity of oxygenated and multifunctional peroxy and oxy radicals.

* The range of NO_3 concentrations in the atmosphere and hence its importance as an oxidizing species for VOC

* The emissions of VOC from terrestrial biogenic and oceanic sources

Future research activities

* Laboratory kinetic and product studies on VOC and their radical intermediates that make full use of new and emerging analytical techniques.

* The continued use of theoretical approaches to probe reaction mechanisms and provide estimates of parameters such as vapour pressure and Henry's Law constants.

* The continued development of detailed chemical mechanisms that evolve with advances in our knowledge of VOC chemistry. Subsequent testing of the mechanisms against data obtained from chamber and field studies.

* Comparison of field observations, including satellite data, with predictions based on laboratory data and models.

1.3. Production, properties, and removal of SOA

Secondary organic aerosol provides the greatest challenge at the current time, both conceptually and experimentally. In the absence of clear characterisation of the species involved and the problems associated with measurements of the composition and properties of the aerosol, it is very difficult to formulate the necessary components required to model SOA adequately. Group 3 listed several key questions with regard to SOA in the troposphere.

* What are the most important precursor VOC for SOA? Are all important SOA precursors identified and taken into account? Are chamber experiments appropriate for ambient air simulations?

* Which processes are most relevant for SOA formation (*i.e.* nucleation, condensation, cloud processing, heterogeneous and multiphase chemical processing)?

* Which processes are most relevant for SOA removal (*i.e.* dry deposition, wet deposition, SOA volatilisation)?

In addition the group pointed out the appreciable shortcomings in model predictions for SOA in the real atmosphere. It was clear that updated parameterizations of SOA formation in models is needed.

Field work

The group recommended that future experimental work should focus on the following.

* Field experiments to test predictions of SOA from biogenic VOC in polluted and clean environments.

* Identification of truly representative SOA precursors from anthropogenic and biogenic sources.

* Laboratory studies to test gas-phase mechanisms of VOC oxidation and multiphase chemistry, particularly with regard to the formation and partitioning of molecular building blocks for SOA, such as small acids, dicarboxylic acids, hydroperoxides, unsaturated aldehydes and glyoxal.

* Development of instrumentation to improve the sensitivity of analytical techniques to detect the low concentrations and more complex molecules in real atmospheric aerosol at a molecular level.

* Studies of the optical, chemical and hygroscopic properties of SOA, and of SOA yields under low NO_x and low VOC precursor concentrations. Attempts should be made to answer the question: can the concentration dependence observed for α-pinene be generalized to other VOC?

Modelling

Future modelling efforts to test novel ideas would be helpful; these need to be developed by experimentalists. It is critical to evaluate further the models with regard to oxidant field and to aerosol composition and properties simulations. In parallel to supporting experimental work, current model development could focus on the following.

* Simulation of size dependence of aerosol composition and properties
* Parameterization of heterogeneous reactions and of multiphase chemistry and their involvement in particulate organic mass formation
* Expansion of the current representation of SOA formation in atmospheric models (volatility controlled gas-to-particle partitioning into a liquid organic aerosol phase) towards solubility-volatility-reactivity controlled partitioning of aqueous/organic multiphase systems.

2. Introduction to the 3rd ACCENT Barnsdale Workshop

2.1. Volatile Organic Compounds in the atmosphere

2.1.1 VOC

Volatile organic compounds (VOC) play a central role in air pollution; they react with nitrogen oxides in the presence of sunlight to generate ozone and other photo-oxidants; they also, in the course of their various reactions, can form higher molecular weight organic compounds which condense to produce "secondary" organic aerosol (SOA).

VOC occur in the natural environment. Methane (CH_4), the simplest and most prominent VOC, is released from microbiological reactions in marshland and stagnant water and, recently, it has also been shown to be produced by forests. Other important naturally occurring VOC include isoprene and a number of terpenes which are released by trees and vegetation. The amounts vary with tree species, with the tree condition, with the season and the temperature.

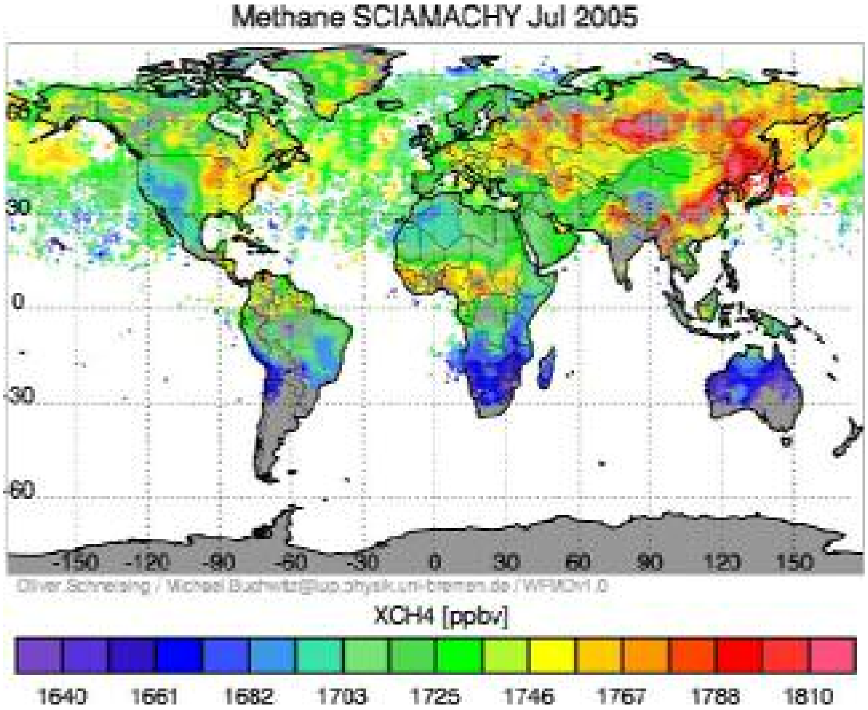

Figure 2.1 Global view of methane mixing ratios in July 2005. Image kindly supplied by Michael Buchwitz, IUP, Bremen.

The largest contribution to human-produced VOC comes from the many hydrocarbons emitted by the oil industry. At every stage from the oil fields themselves, through the drilling, transport, refining and distribution, VOC are lost to the atmosphere.

While VOC are often considered solely in terms of volatile hydrocarbons, there are a whole range of oxygenated compounds (OVOC) as well as many further organic compounds which contribute to the pollution burden of the atmosphere. Many of these are released to the atmosphere from the evaporation of solvents used for painting, coating and in the manufacture of adhesives. In addition, most oxidation products of primary pollutant VOC are themselves VOC.

Apart from CH_4 which has an average mixing ratio in air of 1.75 ppb, VOC usually occur at mixing ratios of a few ppb or less. Real time methods of analysis generally cannot be used, so flask sampling is usually employed to measure VOC. Thus for most ground-based measurements, the time resolution is poor, and the expected diurnal variations in concentration cannot be followed. It is also possible to measure organo-peroxy free radicals indirectly in real time; either by chemical amplification or with laser induced fluorescence. However the measurements always give the sum of the peroxy radicals and cannot distinguish the various species present. CH_4 can be observed spectroscopically, and, as Figure 2.1 shows, it is possible to construct global scale maps using spectroscopic instruments mounted on satellites to show the variation in space and with season.

2.1.2. The degradation of VOC

The main fate of VOC in the atmosphere is reaction with OH, followed by the addition of oxygen to form a peroxy radical, RO_2.

$$RH + OH \rightarrow R + H_2O \qquad (1)$$

$$R + O_2 \rightarrow RO_2 \qquad (2)$$

In a polluted atmosphere, the peroxy radical may then react with nitric oxide, NO, to form NO_2, which, during the day, can then be photolysed, to form an oxygen atom which reacts with O_2 to form ozone.

The further radicals produced in the reaction with NO, react further to form oxygenated VOC (OVOC), and the OVOC will then be attacked by OH, in a similar sequence of reactions. Since the many intermediate radicals formed in the oxidation processes can undergo a plethora of reactions to form other VOC, including undesirable photo-oxidants such as peroxyacetyl nitrate, PAN, ($CH_3COO_2NO_2$), the reaction picture is very complex indeed.

While the main scavenger of VOC in the atmosphere is the OH radical, VOC can be degraded by NO_3 radicals at night, Unsaturated VOC such as ethene can also react directly with O_3. In each case radicals are formed which react further to form other radicals and compounds.

The ultimate fate of VOC in the atmosphere is oxidation to carbon dioxide (CO_2) and water (H_2O). However the oxygenated intermediates formed in the reactions may be soluble and so be rained out. VOC is also lost from the atmosphere by deposition to soils and plants.

2.1.3. Secondary organic aerosol (SOA)

The organic free radicals, produced in the oxidation reactions of VOC, can react in a variety of ways, some of which form less volatile, stable products. These may condense onto aerosol nuclei forming aerosol particles, and the compounds a repartitioned between the gas phase and the liquid/solid phase on the particle. The particles are known generally as secondary organic aerosol (SOA). Their importance has grown in recent years as their existence has been demonstrated, and as the public concern about the potential effects on health of small particles has grown. By their very nature, the detailed chemical composition of SOA is seldom known and the aerosol is very difficult to characterise and quantify.

2.1.4. Difficulties with VOC and SOA

The difficulties with VOC and SOA are those of the number of compounds present in the atmosphere and the vast number of potential reactions which form and remove them.

Despite the excellent measurements of major VOC, it is impossible either to characterise all of them, or to quantify all of those that have been observed. Thus the measurement set is always much less than the total number of VOC present.

For modelling the photo-oxidation and the degradation of VOC in the atmosphere, the sheer number of compounds with the even greater number of potential reactions makes the complete task impossible - the Master Chemical Mechanism lists several hundred VOC and several thousand reactions, and the authors would not claim it to be complete. Within the compilation, few of the reaction rates, temperature dependencies and other parameters, have been measured in the laboratory, so use has to be made of generic mechanisms and parameters which, it is hoped, are representative.

Furthermore the reaction mechanisms themselves are uncertain – the oxidation of the common aromatic hydrocarbons such as benzene and toluene, which have been the subject of numerous laboratory investigations, still have appreciable gaps, both in the species formed and in the simple carbon balance between reactant and the sum of the products.

Thus practical chemical transport models (CTM) cannot encompass even what is known and must resort to simplification. VOC are represented by a few surrogate compounds and their reactions by generic reactions with likely parameters. In view of the uncertainties indicated, practical CTM give surprisingly good results for ozone production and the diurnal cycling of nitrogen oxides.

SOA exacerbates the problems of modelling. Here the species are hardly known, and the representation of nucleation and condensation is difficult to characterise. The practical solution for SOA in models is presently simple parameterisations.

2.2. AVOC: aims and organisation

The 3rd ACCENT expert workshop was initiated to try to address some of the many uncertainties indicated in the previous section, and to indicate research paths by which they could be reduced. The workshop was held under the auspices of seven ACCENT groups: Transport and Transformation of Pollutants (T&TP), Remote Sensing from Space (AT2), Access to Emissions; Access to Laboratory Data, Aerosols, BIAFLUX and Modelling. The meeting was held at the Barnsdale Hall Hotel in Rutland on Monday, Tuesday and Wednesday 30th & 31st October and the 1st November 2007; some forty nine experts attended (*Appendix 1*).

The aims of the AVOC meeting were:

* to identify and review the key uncertainties in our current understanding of the emission to the atmosphere, processing within the atmosphere and removal of VOC from the atmosphere; and

* to provide a basis for future collaborative research priorities in this area.

The meeting was organised around three discussion groups, addressing the major areas of concern.

1. Emissions of VOC – anthropogenic and biogenic.
2. Uncertainties in local, regional and global processing of VOC.
3. Production, properties, and removal of Secondary Organic Aerosol – the fate of VOC.

The meeting (*Appendix 2*) started with a plenary session in which there was an invited review paper on each topic, followed by a short response by the Chairs of each group who formulated the questions to be discussed. The groups then separated for a day. The final combined session was devoted to reports from the Rapporteurs of each of the groups and a general discussion on future directions. All the speakers, chairs, rapporteurs and participants received detailed instructions to try to ensure that the discussions were as productive as possible (*Appendix* 3).

Each participant was asked to submit a brief account of their own contribution for publication. The main burden fell on the three Rapporteurs who, with help from the Chairs, summarised the discussions and formulated the recommendations.

2.3. The arrangement of the report

The essential part of the report is the three contributions from the Rapporteurs of the groups, giving the recommendations of their respective groups. These are followed by a summary and conclusions. The initial overview lectures are given to enable a reader to obtain a perspective on each of the discussion topics. The final section contains the contributions from the individual participants who submitted accounts of their contributions to the discussion.

3. Emissions of VOC – anthropogenic and biogenic

Rapporteur's Summary from Group 1

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Participants: *Jürgen Kesselmeier (Chair), Nicola Blake (Rapporteur), John Burrows, Neil Cape, Cristian Cojocariu, Francesco Loreto, Michela Maione, Malcolm Possell, John Remedios, Stefan Reimann, Gunnar Schade, Dominique Serca, Sheena Solomon, Jochen Theloke, Mihalis Vrekousis, Folkard Wittrock, and with contributions from Claire Granier, Eiko Nemitz and Rainer Steinbrecher (communicated).*

3.1. Introduction

Volatile Organic Compounds (VOC) released into the atmosphere by both anthropogenic and biogenic processes play an important role in the chemistry of the atmosphere. Anthropogenic VOC (AVOC) have been measured in the atmosphere for about the last 50 years [*e.g.* Eggertsen and Nelsen, 1958]. This work has informed public policy initiatives to implement VOC emission control strategies such as the addition of catalytic converters to vehicle exhaust systems.

Likewise, it has been well accepted since the pioneering work of Frits Went [1955, 1960] that biogenic VOC (BVOC) play an important role in the composition and chemistry of the atmosphere. However, the full extent of this role is only just being revealed. Most scientists now agree that annual worldwide emissions of BVOC are more than 10 times greater than those of all AVOC combined.

Within this context, oxygenated VOC (OVOC) have only lately come to the attention of scientists and policy makers, in part because of the development of existing analytical methods, but mostly as the result of the introduction of the new direct ionization mass spectrometer (PTR-MS) measurement technique.

AVOC and BVOC both contribute to photochemical smog, tropospheric ozone changes and secondary organic aerosol (SOA) formation. Therefore, their fate is directly linked to air quality and human health.

In order to evaluate the potential impacts from both AVOC and BVOC, it is essential to understand the processes that determine their emissions, as well as their fate in the atmosphere.

Results of discussions

Group 1 identified several key topic areas that we considered to be important to the understanding of VOC emissions to the atmosphere. They are listed below, along with the principal threads of our discussion and the recommendations that were formulated as a result.

3.2. Anthropogenic VOC emissions

Concentrations of many AVOC have continuously decreased in many urban areas since measurements were first implemented several decades ago, due to the introduction of technical measures to curb emissions, such as the catalytic converter systems for mobile sources and the replacement of organic solvents in industrial and household applications. Even though many US cities have distinct and variable VOC emission signatures, if enough different cities are compared, a pattern of surprisingly similar emission ratios to

CO starts to emerge (Figure 3.1). However, cities in poorly-studied regions, such as Africa, are likely to have very different emission "ecotypes", based on typical fuel use and type different from US cities.

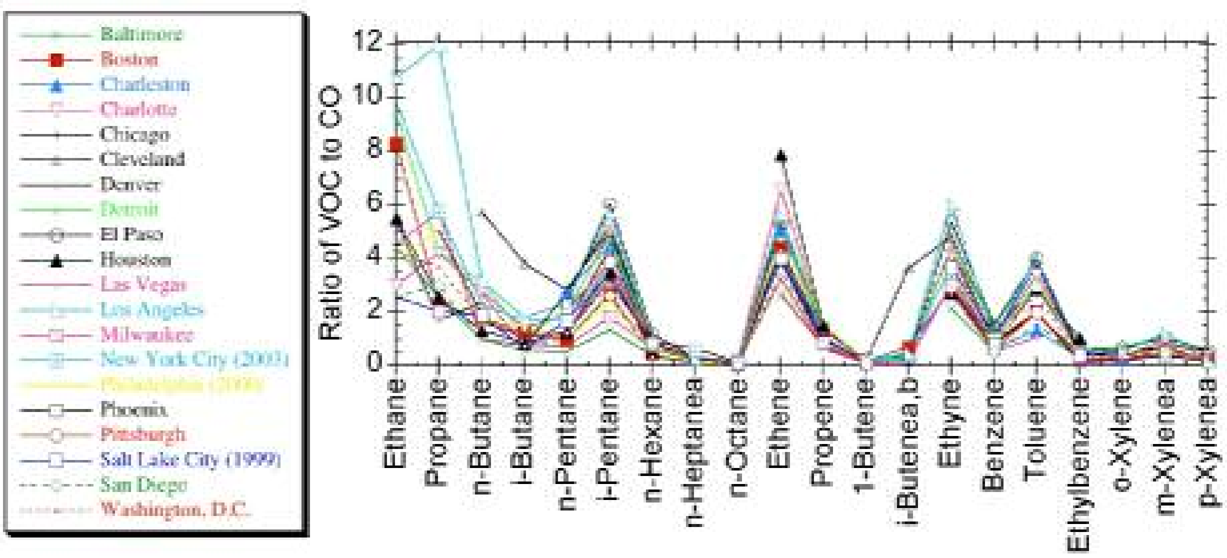

Figure 3.1. Recent (1999-2005) UCI measurements of VOC in 28 US Cities. Ratios to CO for correlations with $R^2 > 0.30$ (most are > 0.60) are plotted. [Baker *et al.,* UC, Irvine, in preparation].

Emissions inventories (EIs) for AVOC still are associated with major uncertainties. Such inventories take time to prepare, and emissions are always changing. Sector distributions also vary greatly, for example industrial versus mobile sources, as well as the seasonal variations of emissions, which must be taken into account to understand the relation of the emissions to the oxidative capacity of the atmosphere and air quality.

The group heard various examples of new analytical techniques that are making important contributions to measuring concentrations and fluxes of a wide range of VOC – including OVOC. New measurements of long chain compounds, emitted by industrial solvent use, are also throwing light on their importance in the production of SOA.

Correct apportionment of VOC between the various emission types is crucial in terms of making policy decisions to regulate emissions. However, the group recognised that this can be a difficult task. It is especially challenging to distinguish between anthropogenic and biogenic sources of, for example, acetone and methanol, and employing isotopes may be a useful tool to tackle this problem.

AVOC research areas prioritised for further study

* Characterize sources, fluxes and variability (diurnal, weekend, seasonal, climate, *etc.*) of AVOC, especially OVOC and long chain compounds. The seasonal variation of solvent evaporative emissions in particular needs to be better characterized.

* Continue to develop, refine and deploy widely new analytical techniques for measuring concentrations and fluxes of AVOC, especially OVOC.

* Make measurements and compare as many different cities as possible to establish city "ecotypes", especially for cities in poorly-studied regions.

* Employ isotope studies to distinguish between anthropogenic and biogenic VOC sources, especially for OVOC.

3.3. Biogenic VOC emissions

Plants exchange with the atmosphere a large number of VOC, several of which play very important roles both in plant physiology and ecophysiology, and in the chemistry of the troposphere. These include volatile isoprenoids which are emitted at very high rates by many plant families. Of these, isoprene (2-methyl 1,3-butadiene) is the most abundant non-methane hydrocarbon in the atmosphere with emissions from plants currently estimated to be at least 500 Tg C y^{-1}, or about half of the total emission of biogenic hydrocarbons. Monoterpene emissions are estimated to be lower than those for isoprene, but probably have a higher uncertainty. Recent emission measurements employing accurate instrumentation indicate the need for continuous revision of the estimates. BVOC emissions are larger but *far* less certain than for AVOC. The ratio of BVOC to AVOC is ~ 10:1 in remote areas and ~1:1 in urban areas.

Isoprenoids are very reactive and this is the reason why they are so important in atmospheric chemistry. The products of their high photochemical reactivity were found to generate ozone episodes around large cities, although the ozone production depends on the appropriate ratio of VOC to NO_x. New measurements reveal that several isoprenoids are also involved in the formation of particulates and aerosols, which are now considered to be among the most dangerous pollutants in urban areas. In addition, isoprenoids may indirectly favour the accumulation of less reactive greenhouse gases, such as methane, by successfully competing with these compounds for the cleansing atmospheric radical OH·.

The group considered that the current BVOC emission inventories are NOT sufficient. It was noted that emissions cannot usually be projected, *e.g.* within plant families, so measurements have to be made individually by species. In addition, many compounds such as the highly reactive sesquiterpenes, are not considered. They are very hard to measure as they oxidise so quickly - within the first centimetres after emission. Nevertheless, they are probably still important in terms of SOA production but, until new techniques are developed to obtain emission estimates accurately and reliably, the group suggested that the BVOC community should perhaps deal with them in terms of the products they form (like SOA and glyoxal) and concentrate on measuring those. Another suggestion was to take an integrated chemical approach to assessing the emissions of such reactive emissions, more in terms of a carbon budget closure experiment. It was pointed out that the compounds are not very volatile and there appeared to be a consensus within the group that the huge emission fluxes that have been proposed are probably not realistic in terms of carbon available from plants.

The group also discussed other factors that need to be considered when making measurements to be included in a BVOC emissions inventory. Many, such as the need to parameterize more than just light and temperature when modelling emissions (Guenther's algorithm), the need for improved QA/QC and supporting measurements, and the need for long term year-round flux measurements, are considered in more detail in subsequent sections.

General BVOC research areas prioritised for further study

* The huge uncertainties in BVOC emissions need to continue to be addressed. Current emission inventories need to be drastically improved.

* Many more compounds need to be considered and there is a need to include all major plant species.

- * Primary emission measurements at branch or leaf level are needed under conditions where fast oxidation reactions of reactive VOC species released are excluded.

3.4. The reaction of BVOC emission rates to various global change scenarios

The biosphere (including the oceans) is already exposed to perturbed conditions caused by, for example, long-term increase of pollutants such as O_3, elevated CO_2 and, especially, changes in land use (deforestation, reforestation, fire, agriculture, *etc*). Climate change can and will change BVOC emissions even more - through changes in temperature, O_3, CO_2, distribution of rainfall (including drought and flooding effects), fire frequency, *etc.* Such feedbacks could impact air quality on a large scale. Very little is known about potential biospheric responses, even for the better-characterized compounds like isoprene. For example, a high CO_2 level decreases isoprene emission but emissions increase with temp (Figure 2). Then for example, how much O_3 can plants take up (scavenge) or tolerate without being damaged? This is highly uncertain and depends on other stressors and VOC in the plant. Methanol and formaldehyde fluxes go up with O_3 stress but this response is also still very uncertain, as is the response of carbonyl emissions. Other new studies using new techniques are giving surprising findings, for example, uptake of increased CO_2 might be offset by effect of O_3 on plants (O_3 stress).

A more complete study of basic physiological processes is needed to understand what is behind plant mechanisms that deal with VOC and especially scavenging. We also expect highly species-dependent responses to climate change, which will probably require the screening of all major species individually, as well as the likely change in spatial distributions of species.

Flux measurements in tropical ecosystems are crucial to our understanding of the potential response of BVOC emission rates, being a region with high emission rates that is already subject to widespread change in land use. Unfortunately, the logistics required to maintain a network of flux towers in the tropics make it a very difficult task.

BVOC responses to climate change: research areas prioritised for further study

- * Long-term year-round BVOC flux measurements are needed, especially for tropical ecosystems for a better understanding of current emissions, and to monitor future changes.
- * Light and temperature alone are not sufficient to predict the response of emissions to global change (Figure 3.2). There is a need to include seasonality, ecophysiology, water availability, *etc*. Circadian controls may also be important for how plants react to change.
- * Basic physiological processes need more intensive work

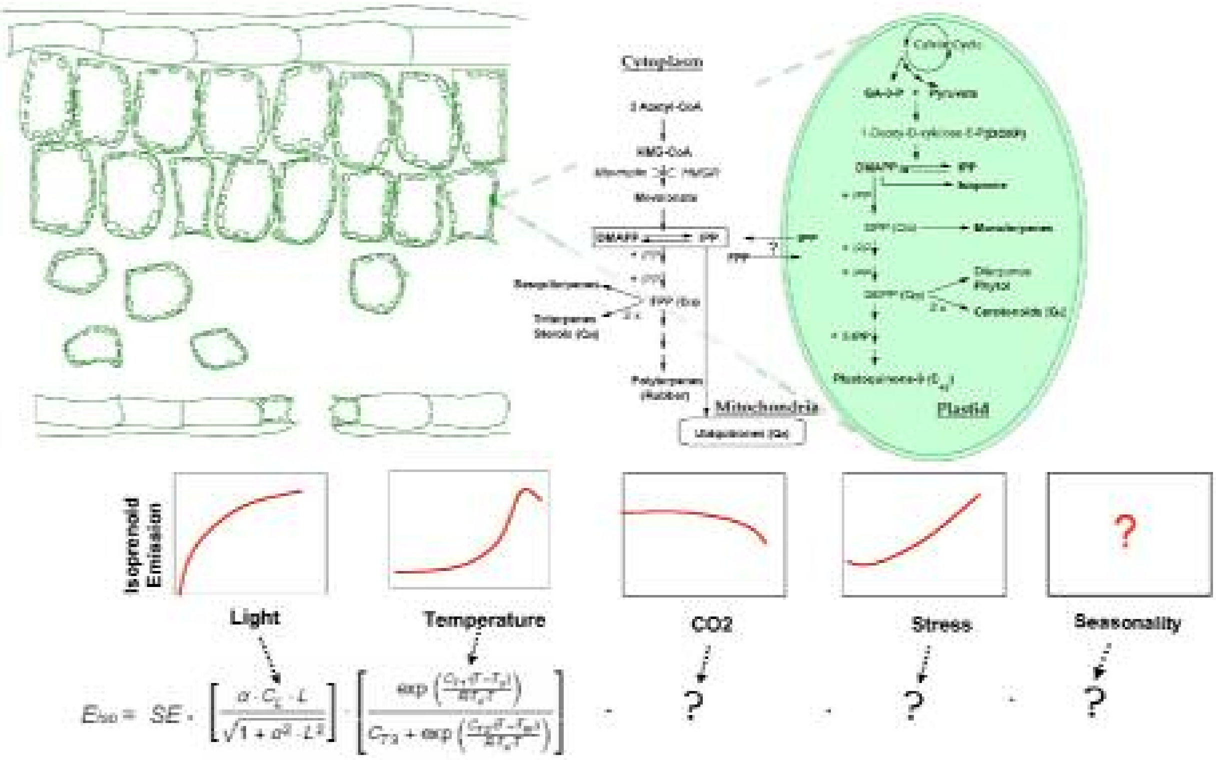

Figure 3.2. Isoprenoid biosynthesis in higher plants and response of isoprenoid emissions to environmental factors.

Plant isoprenoids are synthesized *via* two different pathways (for review see Lichtenthaler [1999]), a cytoplasmic and a plastidic one. Within this context it is well accepted that the volatiles, isoprene as well as monoterpenes, are formed inside chloroplasts from the basic precursor isopentenyl diphosphate (IPP, C_5) and its isomer dimethylallyl diphosphate (DMAPP). The plastidic IPP is synthesized via deoxyxylulose-5-phosphate (DOXP) whereas the cytoplasmic one depends on mevalonate, the precursor for compounds such as sesquiterpenes, triterpenes and polyterpenes or the mitochondrial ubiquinones. Plastidic condensation with additional IPP units forms successively larger molecules, *e.g.* geranyl pyrophosphate (GPP, C_{10}) farnesyl pyrophosphate (FPP, C_{15}), and geranyl geranyl pyrophosphate (GGPP, C_{20}), in addition to isoprene and monoterpenes delivering compounds such as diterpenes, phytol, carotenoids or plastoquinone. The exchange of biosynthetic precursors and product between the two pathways is under intensive investigation [Bartram *et al.* 2006].

The emissions graphs relate the response of the isoprenoid emission to environmental conditions such as light, temperature, CO_2, environmental stress, and seasonal changes. Only the relations to light and temperature are included in the mathematical algorithm (based on Guenther *et al.* [1991, 1995, 1999]), which is usually used to describe the isoprenoid emission (Eiso) and predict the response to photosynthetically active radiation and leaf temperature. Other ecophysiological influences which may be of substantial significance such as CO_2, stresses (including herbivory and pathogens) or seasonality have been experimentally demonstrated but have not been yet included in the algorithm [Kesselmeier and Staudt 1999].

3.5. Improving models

Due to the large number of VOC present in the atmosphere, understanding their atmospheric fate requires the determination of the spatial and temporal variation of selected VOC that can be used as “proxies” for specific VOC categories (for instance anthropogenic or biogenic VOC) and link these VOC tracers with bulk VOC emissions and their fate in the troposphere. The group commended the use of bottom-up, as well as top-down, modelling approaches.

There was consensus within the group that there needs to be much more emphasis within the atmospheric/environmental community on better and more timely archiving of the measurement databases, which are the foundation of modelling and policy recommendations. The group recommended that data contained in any published article cite a link to, and be submitted to, a recognised archive as a requirement of publication.

As noted above, inventory information is continually changing, so we need “living” databases, which are constantly updated and contain information on the strengths and limitations of each measurement.

The group recognised that “Official” emission inventories can be a political problem. Government agencies can not be expected to vet data officially submitted by different countries. “Expert” inventories were suggested as a solution.

All of these activities represent an enormous task. However, continuity is needed to avoid the waste of time and resources associated with having to start over again in response to each new funding initiative, especially after a gap.

Improving models – action items

* Better speciation of AVOC by compounds and emission category is needed, together with more OVOC species. Algorithms (“simple” ones) need to be included for BVOC.
* Funding of emission measurements is needed where there are large data gaps – *e.g.* tropical forest, Africa, South America.
* Need to support primary emission measurements on a plant species level.
* Scientists need to be disciplined with respect to timely and complete submission of their quality-controlled measurement data. Such data need to be submitted to a recognised archive in standard format to be widely accessible for use in models – *e.g.* on ACCENT website.
* Journals should be encouraged to mandate that references to data files secured in a recognised archive accompany any articles that are published.
* There is a need to secure long term resources to maintain a living, expert-validated emission inventory.
* Methodology for model comparisons requires better overlap of species in model emission inventories.

3.6. Improving satellite contributions to VOC emission questions

Observing the atmosphere from space is an exciting field and one that is expanding rapidly. The group heard, for example, about new glyoxal measurements that are just beginning to be interpreted, and how satellite formaldehyde retrievals have good potential for identifying and constraining AVOC and BVOC sources on a global scale. However, it was clear that a great deal of essential work still lies ahead of this community, especially to combine satellite data with validation measurements and with models. Limb measurements provide enhanced vertical resolution. New or planned limb measurements that will be very useful to the atmospheric science community include ethane, ethyne, acetone, PAN, organic acids, and methanol.

It was noted by the group that the success of satellite measurements will be enhanced by long-term terrestrial measurements of VOC, as well as further development of emission inventories and improvements in atmospheric models along the lines already outlined above.

Specific recommendations from satellite discussion

* Continue gathering data and adding measurement capability, for both satellite and terrestrial platforms.

* There is a need for higher spatial and temporal resolution satellite measurements

* Geostationary satellite instruments are needed to capture and account for large diurnal trends in many measured compounds.

* More emphasis should be made on limb measurements because of their better vertical resolution.

* Improvements are needed in the knowledge of basic laboratory spectroscopy to underpin the spectroscopic determination of VOC.

3.7. QA/QC reporting in support of measurement data

The group agreed that to make best and widest use of any VOC measurements, the specific sampling protocol associated with those measurements needs to be reported together with the data. Examples that were presented to the group include the need to include basic micrometeorology with flux measurements. For cities, the sampling sites need to be characterized by the situation (curbside, park *etc.*) and height of the measurement site. Plant species measurement periods should be a minimum of 1-2 days and made at different times of year.

When reporting BVOC flux chamber data, it was noted that it is important, for example, to make a distinction between static versus. dynamic chamber types, whether ozone was present or not, *etc.* All measurements of VOC exchange need to be accompanied by measurements of primary physiology, including CO_2 and water exchange (photosynthesis, respiration, transpiration, stomatal conductance).

The group also stressed the importance of inter-comparisons to validate and standardise measurements. Specific examples that were cited included the need to compare PTRMS instruments, and to exchange standards for gas chromatography work. Such comparisons are not yet routine for many short-lived compounds and OVOC because of the difficulty in preparing reliable and long-lasting standards that can easily be exchanged

QA/QC discussion recommendations:

* All VOC measurements reported to archives need to be accompanied by appropriate supporting sampling protocol information.

* Good QA/QC protocols, for both AVOC and BVOC, need to be supported, including inter-comparisons where possible.

* There is a need to encourage the development of new technology to improve techniques to make and share standards.

3.8. Long-term measurements and regular campaigns

There was unanimous agreement in the group 1 discussions, as well as during the general discussion, that there is a strong need for long-term measurements (defined by the group as ~ 20 years). Such measurements are crucial in assessing the effects of emissions on air quality and global change and to evaluate the success of legislation. They are also useful for satellite validation. Satellite measurements can in turn be used to extend the global coverage of long-term station measurements.

The type and location of long-term measurement platforms needs to be carefully selected for most efficient model/inventory/satellite validation. The group recommended that, for example, the tall tower CO_2 network in Europe and US could provide platforms to extend the scope of remote VOC sampling, but it was agreed that such measurements should not be limited to background stations.

Long-term measurements - action items

* Existing long term measurement platforms should continue to be supported, and the scope of VOC measured should be extended to add new, carefully selected, measurement sites in strategic remote, rural and urban locations. New measurement techniques should be encouraged as they become available.

* Satellite measurements should be developed and used to extend the scale of measurement stations.

* Priority species should be defined – including satellite products and global change compounds. One could build on recommendations for specific gases to measure from recent WMO/GAW workshop. Glyoxal and supporting tracers such as CO, methyl bromide and other halogenated VOC should be added to the list where possible.

* New modelling tools like particle dispersion models should be further developed and employed to interpret measurement data in terms of changing emissions. Back trajectories, by themselves are insufficient,

3.9. Summary of specific recommendations and future outlook

The huge uncertainties in VOC emissions need to be addressed and current accuracy and precision of emission inventories need to be drastically improved. The highest priority identified by the group was BVOC emissions, where many more compounds need to be considered, and there is a need to include all the major plant species. Improvements in mission inventories for OVOC and long-chain VOC were also identified as high priority.

Adequate characterization of VOC emission variability (diurnal, weekend, seasonal, *etc.*) was identified as being crucial to our understanding of current and future emissions. New and existing platforms are required to make high quality science-based (rather than policy-based) long-term measurements. The monitoring stations need to be situated in a wide variety of climate zones and ecosystem types, and in many different urban as well as rural areas. We envisage that satellite measurements will play an important future role to extend the coverage of measurement stations. We have recommended an initial set of compounds to be prioritized.

New analytical techniques need to continue to be developed, refined, and widely deployed to measure concentrations and fluxes of VOC, especially OVOC, long-chain VOC, and reactive BVOC on all platforms, including satellites. New techniques to make and share standards are also needed, thereby facilitating intercomparison and validation of the various VOC measurements.

Data discipline on the part of scientists needs to be encouraged and better access to VOC emissions data needs to be facilitated. This includes the timely submission of measurements and emissions inventories to a recognised archive in standard format, including a standard set of supporting parameters. We recommend that easy access to, and high confidence levels in such archives be promoted by expert-validated website portals such as the one maintained by ACCENT. We further suggest that journals mandate archiving and archive links to accompany all articles as a requirement for publication. Long-term resources need to be secured to maintain a living, expert-validated VOC emission inventory.

Predicting the effects of global climate change factors (such as increases in ambient CO_2, O_3, ambient temperature and response to droughts and flooding) on BVOC emissions is highly uncertain and requires a significantly improved understanding of the biochemistry and physiology of emissions, including updating "Guenther's algorithm". This should be an extremely high priority for future investigation.

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4. Uncertainties in local, regional and global processing of VOC

Rapporteur's Summary from Group 2

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4.1. Introduction

The plenary presentation was given by Jonathan Williams and provided an overview of (i) the uncertainties in emissions of VOC; (ii) the current status of our knowledge of VOC chemistry based on laboratory studies; and (iii) uncertainty in the upper troposphere. Emphasis was placed on the combined role of field measurements and models in identifying areas of greatest uncertainty.

4.1.1 Emissions

Anthropogenic emissions of VOC are not well characterised. The inaccuracy or uncertainty in emissions inventories can give rise to discrepancies between measured and modelled values of the concentration of certain VOC. For example, the measured amount of propane can be up to three times larger than that predicted by models. Emissions inventories can vary and are inherently out of date. They also do not incorporate seasonal dependence in anthropogenic emissions.

Despite their global importance, there is much greater uncertainty in the emissions of terrestrial biogenic emissions of VOC. For example, the measured amount of isoprene in forested areas is often significantly less than that predicted by models. Experimental evidence suggests that this discrepancy is due to a missing source of hydroxyl (OH) radicals. Possible unconsidered sources of OH include aerosol and the ozonolysis of monoterpenes and sesquiterpenes. It was noted that deposition of VOC is generally not included in models and that this may also contribute to the discrepancy between measured and modelled concentrations of VOC.

There is a large uncertainty in emissions of VOC from the oceans. The majority of research in this area has focussed on dimethylsulfide and to a lesser extent on alkanes and alkenes. However there has been very little work on the emissions of oxygenates, despite the fact that they dominate the background atmosphere.

4.1.2 Chemistry

Laboratory studies of the atmospheric degradation of VOC have been used to establish a large kinetic database of relevant reactions. Rate coefficients for the reaction of OH with many VOC are well known and the temperature dependence of these reactions has recently been measured for several simple oxygenates (*e.g.* acetone, methanol) present in the upper troposphere. However, there remains considerable uncertainty in the atmospheric degradation products of VOC at low temperatures and low NO_x concentrations. The products of the reaction of ozone and the nitrate (NO_3) radical with VOC are even less certain and are particularly relevant in light of recent field measurements which indicate that the concentration of NO_3 may be considerably higher then expected. The role of field work in determining uncertainties in our knowledge of

VOC chemistry was highlighted. Measurement of total non-methane organic carbon (C_y) and the total OH reactivity approach provide useful information, but are all of the main relevant VOC measured in these studies?

4.1.3 Upper troposphere

The concentrations of simple oxygenates in the upper troposphere are considerably higher than predicted by models. This is due, at least in part, to missing or inaccurate reaction parameters for the degradation of VOC including photolysis quantum yields as a function of pressure, temperature and wavelength. However, other factors that could contribute to these discrepancies include measurement artefacts (*e.g.* acetaldehyde), the possible role of convection in the transport of trace species and heterogeneous reactions on ice surfaces.

4.1.4. Discussion

The formulation of issues for discussion was initiated by the chairman Ron Cohen. His presentation highlighted several key areas of uncertainty in the processing of VOC, including: (i) the atmospheric degradation of oxygenated biogenic VOC and sesquiterpenes, (ii) the effect of NO_x and HO_2 levels on product distributions and (iii) the reaction of NO_3 with many important anthropogenic and biogenic VOC.

The subsequent group sessions consisted of short presentations from all participants followed by open discussions, which are summarised below.

4.2. Kinetics and mechanisms of VOC oxidation

Laboratory studies have generated a large body of kinetic, product and mechanistic data concerning the atmospheric oxidation of VOC. In particular the kinetics of the initiation step, i.e. reaction with OH, NO_3 and O_3, are now well known for many atmospherically relevant VOC and many of their oxidation products. However, several “knowledge gaps” exist. For primary emitted VOC, the most notable lack of data concerns the reactions of NO_3 with multifunctional unsaturated hydrocarbons and the larger biogenic VOC, including oxygenates. There is also very little kinetic data, particularly for reactions with O_3 and NO_3, at temperatures below room temperature (*i.e.* at temperatures representative of the middle and upper troposphere). Although the atmospheric fate of many of the simple oxidation products (*e.g.* monofunctional carbonyls) has been well characterised, there is a considerable lack of kinetic data for the more complicated multifunctional oxygenated compounds, including nitrates and hydroperoxides. Many of these compounds are not commercially available and are difficult or dangerous to work with. In addition, the structure activity relationships developed to predict rate coefficients for the atmospheric oxidation of VOC tend not to work well for multifunctional species.

However, on a happier note, our knowledge of the reactivity of oxygenated VOC (OVOC) has increased considerably over the last 10 years and a new online database of rate coefficients for the reaction of OH, NO_3, O_3, Cl and Br with OVOC has been established by Laboratoire de Combustion et Systemes Reactifs, LCSR-CNRS, Orleans (http://www.era-orleans.org/eradb). Data is available for reactions of saturated, unsaturated, aromatic, halogenated and nitrogen-containing oxygenates. In the near future, effort will be made to include photolytic quantum yields and a limited amount of mechanistic data. It is also planned that the development/extension of the OVOC database should be closely linked with the Master Chemical Mechanism (MCM) and CODATA/IUPAC databases. The linking of these databases would provide a useful way of bringing together the knowledge gained from laboratory/chamber studies in a way that could feed easily into atmospheric models, using the proposed new MCM tools for mechanism development and simulation of complex chemistry.

Photolysis is also an important atmospheric loss process for carbonyls, nitrates and hydroperoxides. While there has been a steady increase in our knowledge of the photolysis parameters for aldehydes and ketones, more data is needed for multifunctional species, nitrates and hydroperoxides. The recent discovery that the recommended quantum yields for photolysis of acetone under atmospheric conditions may be too large highlights the need for careful measurements of photolysis parameters under a range of relevant pressures and temperatures.

Product data have been obtained for the atmospheric degradation of many important anthropogenic and biogenic VOC. However, these studies have mainly been performed at room temperature in the presence of NO_x, where the intermediate organic peroxy radicals (RO_2) react with NO to produce the corresponding oxy radicals (RO). The degradation of important VOC also needs to be investigated in the absence of NOx, where RO_2 + HO_2 reactions dominate. There is also a considerable lack of data on the effect of temperature and pressure on the yields of oxidation products.

Uncertainties in the mechanisms for VOC oxidation are often due to insufficient knowledge of the fate of the intermediate organic peroxy and oxy radicals. Although the reactions of simple RO_2 and RO radicals appear to be well characterised when R is a small alkyl group, there is a lack of kinetic and product data for oxygenated and multifunctional species. For example the formation yields of organic nitrate ($RONO_2$) in the RO_2 + NO reaction are only known for a few simple alkyl species. Recent experimental evidence has also called into question our current understanding of the reaction pathways in the RO_2 + HO_2 reaction, particularly for oxygenated peroxy radicals. For example, new laboratory studies of the reaction of the acetyl peroxy radical, $CH_3C(O)O_2$, with HO_2 indicate that a radical channel, generating OH, may have a branching ratio as high as 0.4, Figure 4.1.

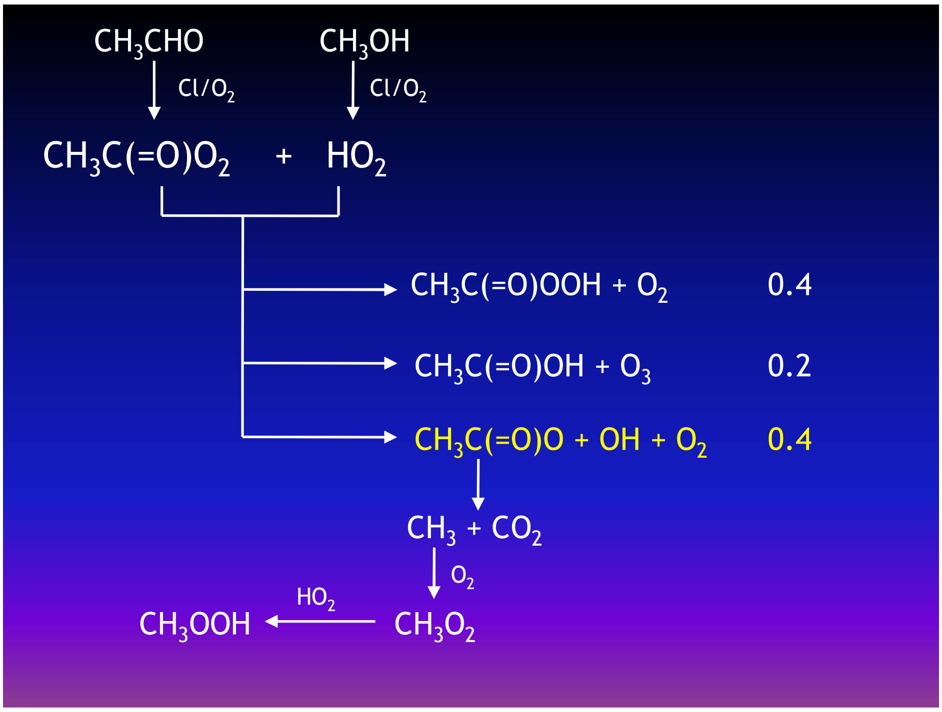

Figure 4.1. Proposed reaction pathways and branching ratios in the $CH_3C(O)O_2$ + HO_2 reaction (presented by Mike Jenkin).

A similar OH radical production pathway has also been observed in the reaction of $CH_3C(O)CH_2O_2$ with HO_2, which suggests that this reaction channel maybe important for oxygenated RO_2 in general. The main atmospheric implication of this finding is that reaction with HO_2 appears to be a less efficient chain terminating process for certain oxygenated RO_2 radicals in the atmosphere than previously thought. This may alter our assessment of processes controlling ambient radical concentrations under NO_X-limited conditions. Clearly further work is needed on the reactions of other oxygenated RO_2, *e.g.* those produced from reactions of OH with isoprene and monoterpenes.

There is also recent experimental evidence which suggests that alternative pathways are available to the intermediate acyl (RCO) and acyloxy (RC(O)O) radicals, produced during the atmospheric oxidation of aldehydes, particularly when R is not a simple alkyl group. Acyl radicals may undergo prompt decomposition to produce R + CO, whilst large acyloxy radicals could isomerise to produce carboxylic acids. Experimental and theoretical studies of these reactions need to be performed for a variety of functionalised aldehydes in order to determine their potential importance.

4.3. Application of explicit chemical models

The development of explicit chemical schemes is necessary to test our current understanding of VOC processing in the atmosphere. Models such as the MCM incorporate rate coefficients and branching ratios for all the relevant chemical reactions and can involve tens or hundreds of thousands of individual reactions. Structure reactivity relationships are used to determine rate coefficients and branching ratios if experimental data is not available. Data obtained from a study of the photo-oxidation of octane using a more detailed and complex model, the self generating master mechanism (SGMM), are shown in Figure 4.2.

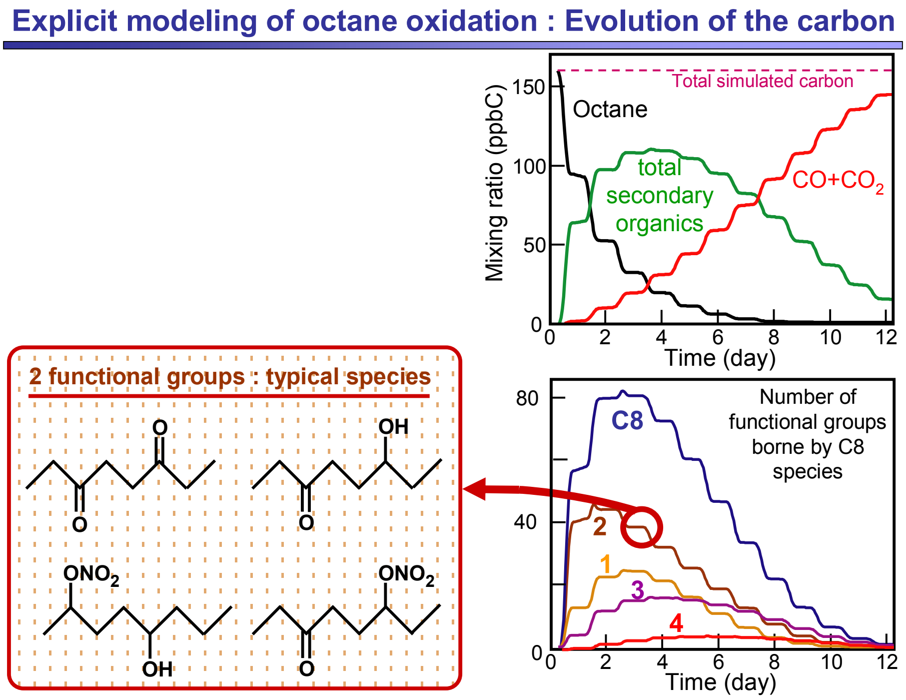

Figure 4.2. Chemical model of the evolution of organic carbon during the photo-oxidation of octane, illustrating the range of multifunctional species produced (presented by Bernard Aumont).

The results indicate that a very large range of multifunctional secondary organics are produced. This is in contrast to the MCM where organic products are dominated by mono or bi-functional species. The difference is probably due to the fact that even a large mechanism like the MCM neglects many reaction pathways that individually make only a minor contribution and performs some lumping to represent secondary species using surrogates. The net result is that the SGMM and MCM produce a different distribution of nitrogen containing species, which in turn leads to differences in the amount of ozone predicted by the two models.

Concentration-time data generated by models such as the MCM can be compared with results obtained from simulation chamber experiments in order to validate VOC oxidation mechanisms. The comparison of modelled and measured data for toluene indicates that there is a missing source of OH in the model, NO_2 is not removed rapidly enough and the amount of ozone is over-predicted. This appears to highlight the fact that, despite several decades of research, there are significant deficiencies in our knowledge of the atmospheric oxidation of aromatic hydrocarbons, one of the most important classes of anthropogenic VOC. On the other hand, it also raises the question of whether these observations from chamber experiments are relevant to the atmosphere. Ultimately, this is an example of the complexity of VOC oxidation and illustrates the need for a combined laboratory/modelling/field measurement approach in addressing uncertainties in our knowledge of the processes involved.

4.4. New techniques, field measurements and global models

New and emerging analytical techniques can play an important role in our efforts to understand the degradation of VOC in the atmosphere. The new generation of mass spectrometric techniques, in particular, have proved to be extremely useful in the identification of reaction products and intermediates in both chamber and field studies. For example, it has recently been demonstrated that the technique of CIR-TOF-MS can be used to distinguish between the isoprene oxidation products methacrolein and methyl vinyl ketone, a long-standing problem for mass spectrometric methods. Because of its high sensitivity and time resolution, CIR-TOF-MS also offers real potential in identifying the key intermediate species involved in the formation of secondary organic aerosol (SOA).

Organic acids are known to be important constituents of SOA. However, measurements of these species have proved to be challenging because of their semi-volatile behaviour, *i.e.* they partition between the gas and particle phases. A new technique, which employs a wet effluent diffusion denuder aerosol collector (WEDD/AC) coupled to an ion-chromatograph, has recently proved to be successful in obtaining on-line measurements of the gas-particle partitioning of up to 20 organic acids in chamber and field studies. The information generated in these studies may be used to elucidate the role of organic acids in SOA formation.

Field measurements of VOC and associated species (OH, NO_x, O_3 *etc.*) are essential in order to compare observations in the real atmosphere with predictions made from experimental laboratory data. Measurements of the spatial and temporal dependence of VOC concentrations, combined with emissions estimates and knowledge of the reactivity of individual VOC, can provide extremely useful information on VOC oxidation processes under atmospheric conditions. For example, detailed analysis of a large number of measurements of non-methane hydrocarbons at various sites around the North Sea in the mid 1990s during the HANSA project have been used to show that the efficiency of NO_3 radical chemistry and hydroxyl radical chemistry over northwest Europe are similar in springtime. An average night-time NO_3 mixing ratio of the order of 400 ppt was calculated, which indicates that the NO_3 initiated oxidation of many unsaturated hydrocarbons can be more efficient than OH oxidation, especially outside the summer season.

Valuable information can also be obtained from long-term monitoring of VOC concentrations. The Global Atmospheric Watch (GAW) Programme employs a network of sites to determine the global distributions and trends in VOC composition. Data obtained from the site at Hohenpeissenberg indicate a decrease in concentration of several anthropogenic VOC since the late 1990s, Figure 4.3. Uncertainties in the concentrations of VOC measured at the various GAW sites have been determined from intercomparison exercises and the results indicate a good level of compliance with the quality objectives defined within the GAW programme.

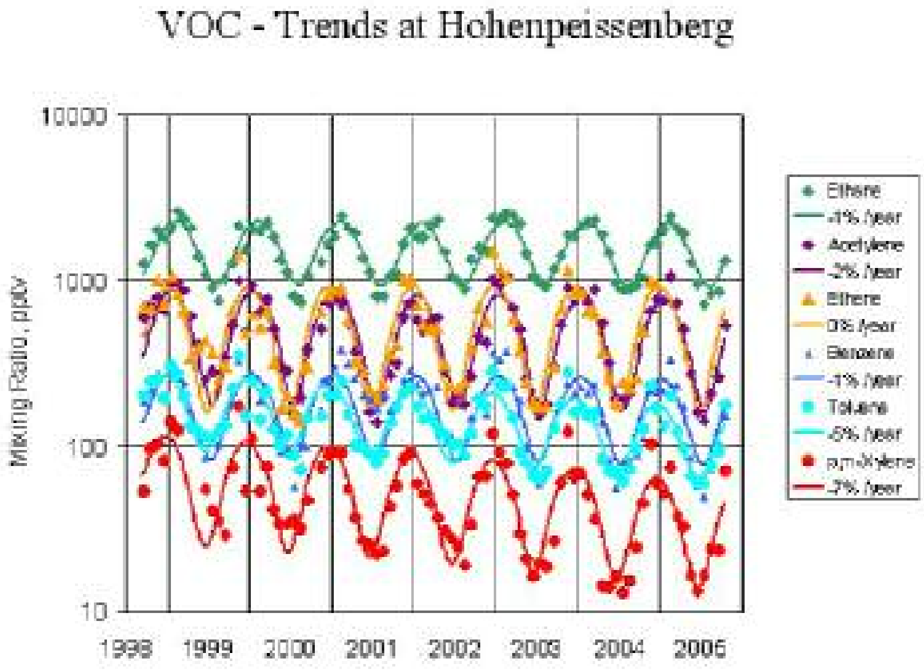

Figure 4.3. Concentration trends for some VOC measured at Hohenpeissenberg (presented by Christian Plass-Dülmer).

Satellite measurements are being used to provide information on the global distribution of oxygenated VOC (formaldehyde and glyoxal) in order to improve our knowledge of the emissions and chemical fate of VOC in the atmosphere. The distribution of formaldehyde and glyoxal are very similar indicating common sources. The regions with large biogenic emissions have the largest local column amounts. However, for selected areas and time periods, biomass burning also produces significant amounts of both, glyoxal and formaldehyde. Interestingly, high column concentrations of these oxygenated VOC also appear over some oceanic areas. This may be due to *in situ* production from long-lived precursors or an oceanic source. Further investigations are currently in progress.

One application of the satellite measurements is to compare the global concentrations of VOC with those predicted by global models. This can help to identify the key uncertainties in the current representation of VOC emissions and chemical processing in global models. Current models of global tropospheric chemistry include simplified schemes of hydrocarbon oxidation, and the uncertainty in the results is large. Recent global chemistry-transport model (CTM) intercomparison exercises have revealed large differences between models in their chemical budgets for ozone and methane and treatment of hydrocarbon chemistry makes a major contribution to these differences.

4.5. Conclusions and recommendations

The group recognised that, in trying to understand the atmospheric degradation of VOC, it is unrealistic to separate chemical processes generating oxidants (*e.g.* ozone, nitrates) from those which lead to the formation of SOA, since both are products of the same chemical processes. The formation of oxidants and SOA are influenced by many of the same factors (*e.g.* sources and sinks of free radicals) and both respond to changes in atmospheric conditions (*e.g.* temperature; level of NOx). A full appraisal of their formation and the responses to changing atmospheric conditions must therefore be based on a sound understanding of the explicit elementary processes involved.

It was also recognised that the representation of such processes in the majority of atmospheric models needs to be substantially simplified. The group was of the opinion that it is essential to establish a sound methodology which allows fundamental information from laboratory and theoretical studies of elementary reactions to feed through to appropriate reduced mechanisms, and that this must initially involve the development of validated explicit (or near-explicit) mechanisms which can respond to new fundamental information. The detailed mechanisms can then provide benchmarks for the development of the reduced mechanisms with resultant traceability to the fundamental information.

Kinetic and mechanistic information related to the atmospheric oxidation of VOC are continuously being produced. Although some of the most important kinetic data is recorded in evaluated databases (*e.g.* IUPAC sub-committee on gas kinetics), the reactions of many VOC are not included at all. The group recommended that a new community-wide approach is required to produce a comprehensive current database of all relevant kinetic and mechanistic information. This needs to be coordinated on an international level and may require the assistance of publishers, as in other scientific areas, to ensure that reported data are inserted into a database at the time of publication.

The following specific uncertainties in the local, regional and global processing of VOC were identified.

* The variation in VOC oxidation product distributions as a function of temperature and also at low NOx concentrations.
* Kinetics and mechanisms for the reactions of NO_3 with multifunctional unsaturated hydrocarbons and large biogenic compounds.
* Mechanistic information for key anthropogenic compounds (aromatics and alkanes > C_5).
* Kinetics and mechanisms for the atmospheric degradation of nitrates, hydroperoxides and multifunctional organics.
* The reactivity of oxygenated and multifunctional peroxy and oxy radicals.
* The range of NO_3 concentrations in the atmosphere and hence its importance as an oxidizing species for VOC.
* The emissions of VOC from terrestrial biogenic and oceanic sources.

Future research activities directed toward reducing these uncertainties should use a multi-faceted interactive approach involving:

* laboratory kinetic and product studies on VOC and their radical intermediates that make full use of new and emerging analytical techniques;
* the continued use of theoretical approaches to probe reaction mechanisms and provide estimates of parameters such as vapour pressure and Henry’s Law constants;
* the continued development of detailed chemical mechanisms that evolve with advances in our knowledge of VOC chemistry. Subsequent testing of the mechanisms against data obtained from chamber and field studies; and
* comparison of field observations, including satellite data, with predictions based on laboratory data and models.

5. Production, properties, and removal of Secondary Organic aerosol – the fate of VOC

Rapporteur's Summary from Group 3

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5.1. Definition of SOA

Secondary organic aerosol (SOA) is defined as the organic aerosol mass formed in the atmosphere by gas-to-particle partitioning of semi-volatile products of the atmospheric oxidation of organic vapour. However, in the following discussion we extend this term to the whole organic particulate mass that is being generated by all types of chemical processing in the atmosphere. Thus, SOA sources include gas-to-particle partitioning in the organic- and aqueous phase, organic phase processing, aqueous phase processing, and multiphase processing (*i.e.* surface, bulk).

5.2. Relevance of SOA for atmospheric chemistry and climate

The state of the art of our understanding of secondary organic aerosol (SOA) formation in the atmosphere has recently been reviewed by Kanakidou *et al.* [2005] and Fuzzi *et al.* [2006]. SOA is relevant on local to global scales. Under favourable conditions, VOC oxidation can act as a source for both gases like ozone, a pollutant affecting human health and ecosystems and a greenhouse gas, and organic particulate matter, and SOA that is expected to exert a cooling of the atmosphere. SOA formation is linked with debates about air quality, visibility, public health, climate, and the oxidative capacity of the atmosphere. Recent experimental findings indicate SOA contributes about 30-60 % of the organic component of the aerosols (OA) in urban air, and >70 % of OA in rural air and the free troposphere [de Gouw *et al.*, 2005; Heald *et al.,* 2005; Johnston *et al.,* 2006; Volkamer *et al.*, 2006; Takegawa *et al.*, 2006; Lanz *et al.*, 2006; Szidat *et al.*, 2006; Gelencser *et al.*, 2007]. The contribution of SOA to aerosol optical density (AOD) is estimated to be larger than that of primary organic aerosol (POA) or black carbon (BC) (Tsigaridis *et al.,* 2006). This contribution is likely to increase as *(a)* current SOA models significantly underestimate SOA production [de Gouw *et al.*, 2005; Volkamer *et al.,* 2006], *(b)* current regulations are likely to result into a reduced contribution of sulphate in the future, while *(c)* SOA precursor emissions could continue increase [Tsigaridis and Kanakidou, 2006].

However, the large number of volatile organic compounds (VOC), the complexity of chemical reactions involved in SOA formation and organic aerosol ageing, and the associated gaps in our knowledge prohibit an accurate representation of the SOA, its occurrence, fate and impacts in chemistry, transport and climate models. Novel experimental results on the production and properties of SOA are emerging and could elucidate key questions with regard to SOA in the troposphere, such as:

* What are the most important SOA precursor VOC?

- Which processes are most relevant for SOA formation (*i.e.* nucleation, condensation, cloud processing, heterogeneous and multiphase chemical processing)?
- Which processes are most relevant for SOA removal (*i.e.* dry deposition, wet deposition, SOA volatilisation)?

5.3. What are the most important SOA precursor VOC?

SOA global model simulations indicate that biogenic VOC oxidation is the major global source of SOA and that this source has been enhanced anthropogenically due to the increases in oxidant and primary particles levels [Kanakidou *et al.*, 2000; Chung and Seinfeld, 2002; Tsigaridis *et al.*, 2006]. It is noteworthy that different models agree with respect to the importance of biogenic VOC for SOA formation over Europe [Andersson-Skoeld and Simpson, 2001; Schell *et al.*, 2001; Tsigaridis and Kanakidou, 2003; Andreani-Aksoyoglu *et al.*, 2007; Simpson *et al.*, 1997] and on global scales [Griffin *et al.,* 1999; Kanakidou *et al.*, 2005]. These model results are in general agreement with ^{14}C measurements that indicate the large contribution of modern versus fossil fuel carbon to organic aerosol over Europe, particularly during summer [Gelencser *et al.,* 2007; Szidat *et al.*, 2006]. Synergistic use of various tracers can provide insight to the SOA occurrence and fate in the atmosphere. The CARBOSOL Project [Legrand, 2006; Legrand and Puxbaum, 2007; Gelencser *et al.*, 2007] has used such tracers (*i.e.* ^{14}C measurements to separate modern from fossil carbon; cellulose as indicator of the biological particles; levoglucosan for biomass-burning and OC/EC to track the primary emissions). The finding of mostly modern carbon is consistent with previous observations [Klinedinst and Currie, 1999, Lanz *et al.*, 2006, Szidat *et al.*, 2006]. Models can reproduce some smog-chamber results [Kamens and Jaoui, 2001]. However, generally, models tend to substantially under-predict atmospheric SOA [de Gouw *et al.*, 2005; Heald *et al.*, 2005; Johnston *et al.,* 2006; Volkamer *et al.*, 2006]. Further, the observation of elevated OA to correlate with anthropogenic pollution [de Gouw *et al.*, 2005; Volkamer *et al.*, 2006], but not with high concentrations of biogenic SOA precursors [de Gouw *et al.*, 2005] presents a currently unresolved conflict with the ^{14}C measurements.

Simpson *et al.* [2007] were able to make use of the CARBOSOL data to confirm that the contribution of primary emissions was captured fairly well by the EMEP model. In Europe, modelled and observed TC matched rather well at northern European sites, but measured SOA components were much greater than the model was able to reproduce at the southern-central European sites, where larger anthropogenic contributions are expected.

Consistent with previous modelling studies, Schaap *et al.* suggested that updating the LOTOS-EUROS model found SOA to be largely from biogenic origin over Europe. They point out the limitations of the modelling studies that are based on land-use data, available only as highly condensed information, which may lead to large uncertainties in the simulated distributions of SOA over Europe.

Similar model results have been presented by Andreani-Aksoyoglu *et al.* [2007] using the MM5/CAMx model to study anthropogenic and biogenic SOA, and temperature sensitivities of SOA formation in the northern and southern parts of Switzerland. They evaluated the contribution of biogenic sources to SOA at about 70 % in the north, 40 % in southern Switzerland and even lower in northern Italy (15-25 %).

Myriokefalitakis *et al.* investigated the SOA production from isoprene using the global chemistry transport model TM4 and found that isoprene enhances the global production of SOA from biogenic VOC by 60 %. This is about 1.5 times higher than recent estimates from a different CTM. Based on chamber experiments, benzene is also estimated to be responsible for up to 40 % of SOA production from anthropogenic VOC.

Hoyle *et al.* using the global OSLO-CTM2 model evaluated that the NO_3 radical initiated oxidation of monoterpenes can account for just over 30 % of the annually averaged global SOA burden. NO_3 oxidation has the largest contribution to SOA formation in heavily populated regions. The anthropogenic influence on NO_3 levels may thus have a significant impact on SOA formation from biogenic VOC.

5.4. Significant shortcomings in SOA predictions for the real atmosphere

Secondary organic aerosol (SOA) formation from partitioning of semi-volatile and non-volatile products of VOC oxidation is being parameterized in state-of-the-art atmospheric models in different ways. Models differ on the considered substrates for the condensation of SOA as well as the surrogate VOC compounds considered that form SOA precursors and have different treatment of the evaporation and condensation [Kanakidou *et al.,* 2005; Robinson *et al.*, 2007]. Many models, for simplicity, parameterise SOA formation based on empirical fits to chamber data.

The accurate simulation of SOA formation in the atmosphere has recently being questioned as a growing body of evidence shows large discrepancies in a comparison of model results with observations in different and large compartments of the atmosphere, including polluted urban air [Volkamer *et al.*, 2006], the outflow of pollution sources [de Gouw *et al.*, 2005; Johnson *et al.*, 2006] and compartments of the free troposphere [Heald *et al.*, 2005]. Given the magnitude of underestimation of SOA production from current SOA models (a factor 5 to 100) we can have little trust that we understand the sources of SOA. While laboratory chamber studies have not been carried out over a sufficient parameter range to provide generally applicable empirically-based representations of SOA formation in complex air masses, the experimental conditions probed in chambers approximate well to the polluted urban atmosphere with regard to VOC, NO_x, OH, O_3 concentrations, light-conditions, and oxidation time scales, differences exist in terms of the pre-existing aerosol and VOC precursors considered [Volkamer *et al.*, 2006]. Considerable uncertainty exists already on very short oxidation time-scales, comparable to time-scales that are being probed in simulation chambers, and these differences increase with photochemical age (Figure 5.1). The significant gaps in our understanding of SOA formation are a priority topic of current atmospheric chemistry research.

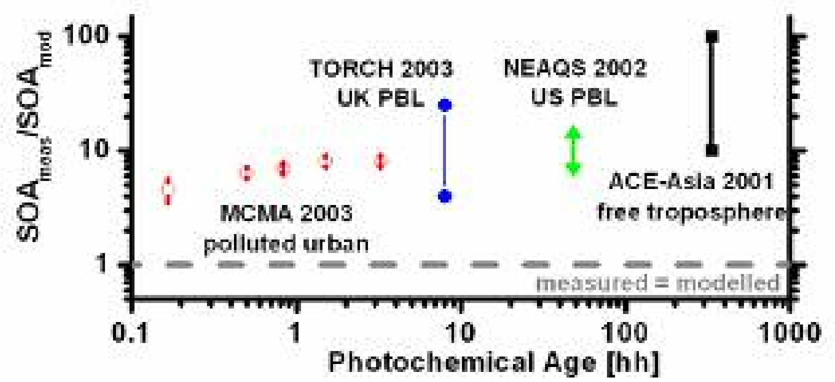

Figure 5.1. Differences in predicted and modelled SOA formation from four field campaigns: NEAQS 2002 [deGouw *et al.,* 2005], ACE-Asia 2001 [Heald *et al.,* 2005], TORCH 2003 [Johnson *et al.,* 2006], MCMA-2003 [Volkamer *et al.,* 2006], reproduced with permission from *Geophys. Res. Letters.*

A number of recent chamber, field and modelling studies provided some insight into this missing knowledge and the gaps in our understanding of the fate of VOC and SOA formation and properties in the troposphere. Isoprene and benzene have been positively identified as SOA precursors [Kroll *et al.,* 2005; Martian-Reviejo and Wirtz, 2005]; oligomer and polymers of oxidized organics, detected on aerosols during VOC oxidation and also on ambient aerosols, have lower vapour pressures than the parent compounds, thus enhancing SOA formation [Kalberer *et al.*, 2004; Gao *et al.*, 2004]; it has also been proposed that multiphase chemistry affects the particulate organic mass in the atmosphere [Limbeck *et al.*, 2003; Gelencser and Varga, 2005; see also discussion in Kanakidou *et al.*, 2005].

5.5. Limitations in experimental studies

Are all important SOA precursors identified and taken into account? Are chamber experiments appropriate for ambient air simulations?

The SOA formation from biogenic VOC has been widely studied in terms of *a*-pinene, primarily because of the higher abundance of *a*-pinene in comparison with other biogenic VOC in rural environments. It was pointed out by McFiggans *et al.* (this workshop) that high atmospheric concentrations of *a*-pinene reflect the fact that *a*-pinene is significantly less reactive than other monoterpenes and sesquiterpenes, and thus *a*-pinene may accumulate in rural air masses rather than contribute appreciably to SOA by oxidation when compared to the more reactive VOC. In recent chamber experiments, McFiggans *et al.* detected a dependence of SOA yields on the concentration of *a*-pinene. Lower SOA yields are being observed with initial concentrations approaching atmospheric levels. Extrapolating their findings to the atmosphere would further lower the SOA production from *a*-pinene over current model predictions. For studies on a molecular level that can provide insight to the SOA occurrence in the atmosphere, cyclohexene, a symmetric proxy for *a*-pinene, is used to simplify SOA formation from biogenic VOC (Alistair Lewis *et al.*, this workshop). Johnson *et al.* pointed out a peculiarity in the oxidation pathways of cycloalkenes that may complicate meaningful extrapolations to endocyclic terpenes: during cycloalkene ozonolysis the yields of stabilised Criegee intermediate varies with the yields of OH in a different way to that observed for acyclic biogenic VOC (most monoterpenes). This may point to differences in the decomposition pathways of the cycloalkene Criegee intermediates (*i.e.* other than the .OH-forming hydroperoxide channel). The information about the gas-phase oxidation pathways presents crucial prerequisite information to identify meaningful proxies for anthropogenic and biogenic VOC.

Metzger *et al.* (this workshop) suggest that the most abundant biogenic hydrocarbon, isoprene, may have been also overestimated as a SOA precursor. In their recent simulation chamber studies, conducted in humidified and dry air, they observe lower SOA yields and – in contrast to previous studies – they do not detect SOA formation when 200 ppb of isoprene are oxidized using H_2O_2 as a radical source.

Similarly, for anthropogenic VOC (AVOC) Volkamer *et al.* (this workshop) pointed out that use of trimethylbenzene as a proxy may be favourable due to its high reactivity (which makes it relatively easy to study in simulation chambers) but the contribution from trimethylbenzene to global SOA from AVOC is relatively small compared to, for example, benzene, as suggested by Myriokefalitakis *et al*., which is much harder to study in chambers due to its reduced reactivity. The differences in SOA predictions and observations on short oxidation time-scales [Volkamer *et al*., 2006] also suggest that accessible time-scales are not a fundamental limitation to obtain atmospherically relevant results about SOA formation with existing laboratory infrastructure.

Recent studies by Donahue *et al.* [2006] proposed a new class of compounds (so-called "intermediate volatility" VOC, or IVOC) as SOA precursors in the urban atmosphere. The identity of IVOC is presently not clear. Since this workshop, it has been demonstrated that a dynamic representation of POA (primary organic aerosol), *i.e.* accounting for the evaporation of low-volatility POA material, its chemical transformation in the atmosphere, and re-condensation of products, significantly alters POA/SOA ratios, and the distribution of OA on regional scale [Robinson *et al*., 2007]. Several contributions presented recent experimental data that call into question whether the right SOA precursors VOC have been studied to date, and point to possible alternatives.

However, other recent studies question the widely established view that the number of carbon-atoms (volatility of products) is a determining parameter for VOC to act as SOA precursors. Volkamer *et al.* [2007] observed SOA formation from acetylene. Acetylene is the smallest hydrocarbon after methane. These results also suggest the aqueous aerosol phase, currently ignored, as a chemical reactor for SOA formation.

5.6. New experimental approaches to characterize SOA formation

5.6.1 Molecular versus macroscopic level

Lewis *et al.* show some results on SOA formation from the ozonolysis of oleic acid and cyclohexene and give some hope that a framework for SOA treatment on a molecular rather than macroscopic level can at least be conceived. In both levels of reaction systems oligomer formation inside the organic aerosol is observed and can be rationalised in terms of combinations of a reasonably small subset of building block compounds (mostly small acids). Future challenges of using molecular structure identification to determine reaction pathways of SOA formation face demands in organic synthesis and improvements in the sensitivity of analytical techniques to detect the low concentrations and higher complexity of molecules in the real atmospheric aerosol.

5.6.2. Building blocks approach

Understanding the chemical pathways of SOA formation in simulation chambers in combination with detailed chemical modelling was shown by Johnson *et al.* to be a prerequisite to identify building blocks of accretion reactions that are likely to participate in SOA formation (*e.g.* hydroperoxides, unsaturated aldehydes). Thus, targeted experimental work is needed, such as that by Johnson *et al.* focusing on testing detailed mechanisms for predicting dicarboxylic acids from cycloalkene ozonolysis, which are known to participate in SOA formation.

5.6.3. Volatility and hygroscopicity combined simulation chamber studies

Simulation chamber experiments of SOA formation from isoprene by Metzger showed that when SOA formation was observed, the aerosol volatility continually decreased over the course of several hours and this was attributed to oligomerization reactions inside aerosols. Aerosol Mass Spectrometer (AMS) results suggest carbonyl-containing compounds and monoacids might be more likely building blocks for SOA compared with multifunctional acids. The use of Volatility Tandem Differential Mobility Analyzer (VTDMA) and Volatility Humidity Tandem Differential Mobility Analyzer (VHTDMA) techniques to characterize the hygroscopic properties of SOA were highlighted.

McFiggans, studying the hygroscopic properties of SOA produced by *a*-pinene, found that SOA growth factors strongly depend on the initial *a*-pinene concentration. SOA generated from 10 ppb of *a*-pinene takes up twice as much water as SOA generated from several hundreds ppb of *a*-pinene. The growth factors also increase over time. Over several tens of hours, this may lead to an additional 50 % increase in the water uptake. Both effects are likely to be due to changes in the aerosol chemical composition as a result of gas-to-particle partitioning and heterogeneous reactions. The lower SOA yields found at lower initial concentrations of *a*-pinene are more representative of atmospheric conditions and will lead to lower estimates in SOA production from biogenic VOC.

The data from Volkamer *et al.* demonstrated that glyoxal partitioning to aqueous aerosols is three orders of magnitude higher than in water; it is reversible, a function of aerosol chemical composition and of relative humidity, and is lower for acidified seeds. As a result gas-phase glyoxal concentrations are significantly affected by aerosols, not just by clouds. The glyoxal oxidation in aerosols requires further study.

5.7. Updated parameterizations of SOA formation in models needed

Due to extraordinary high computing requirements (calculation time, memory) simplifications have to be made in the global aerosol-climate models with respect to predictions of:

- aerosol mass and number concentration;
- aerosol chemical composition; and
- aerosol size distribution.

Hendricks *et al.* (this workshop) highlighted the primitive status of SOA parameterisation in aerosol climate models. The continuously growing capability of supercomputers enables the expansion of the representation of organic aerosol components in the aerosol-climate models like ECHAM4/MADE [Lauer *et al.,* 2005; Lauer and Hendricks, 2006] from the one compound currently used to about ten compounds in the future. The decisions on which species to include and how to represent SOA (mass, number, direct and indirect climate effects, chemical reactivity) depend on the target questions to be addressed and require *a-priori* information on the effects of SOA on local and global scales. Uncertainties in our current understanding of the production, properties and removal of SOA limit the knowledge of how best to expand global aerosol models efficiently.

The involvement of SOA in the formation and growth of particles has also been to taken into account in global models. Grini *et al.* started developing a box-model to implement previous work from Kulmala *et al.* [2004], to calculate the influence of condensable material on the aerosol size distribution. The model explicitly calculates evaporation and condensation fluxes, and minimizes the bias from existing feedbacks of photochemistry and aerosol dynamics in determining the aerosol number distribution. Preliminary results demonstrate that thermodynamic equilibrium is reached on shorter time-scales in the smaller size-bins. Future work aims to calculate nucleation and coagulation rates, and coupling with global models.

The experimental results by McFiggans *et al.* and Volkamer *et al.* indicate that the expansion of the current representation of SOA formation in atmospheric models (volatility controlled gas-to-particle partitioning into a liquid organic aerosol phase) should be towards solubility-volatility-reactivity controlled partitioning of aqueous/organic multiphase systems. Based on the findings by McFiggans *et al.* and Volkamer *et al.* an expansion of similar efforts like those by Myriokefalitakis *et al.* towards other carbonyls and the aerosol aqueous phase is advisable.

It further remains to be tested [Donahue *et al.*, 2006; Robinson *et al.,* 2007] if the concept of SOA formation from the oxidation of intermediate volatility vapours from diesel sources can indeed explain the full amounts of SOA formation in case-studies of the urban atmosphere where SOA observations are available.

5.8. Recommendations for further action

Recent testing of SOA models has demonstrated that large gaps in our understanding of SOA formation inhibit meaningful SOA predictions in the atmosphere. Several field datasets exist that now allow such testing of model performance in and/or downwind of polluted atmospheres. Further, considerably less field measurements exist in areas that enable testing of SOA formation from biogenic sources in a clean (natural) environment.

Future experimental work should focus on:

* field experiments to test predictions of SOA from biogenic VOC in polluted and clean environments;
* identification of truly representative SOA precursors from anthropogenic and biogenic sources;
* laboratory studies to test gas-phase mechanisms of VOC oxidation and multiphase chemistry, particularly with regard to the formation and partitioning of molecular building blocks for SOA, such as small acids, dicarboxylic acids, hydroperoxides, unsaturated aldehydes and glyoxal;
* development of instrumentation to improve the sensitivity of analytical techniques to detect the low concentrations and more complex molecules in real atmospheric aerosol at a molecular level; and
* study the optical, chemical and hygroscopic properties of SOA and SOA yields under low NO_x and low VOC precursor concentrations. Can the concentration dependence observed for α-pinene be generalized to other VOC?

Future modelling efforts to test novel ideas need to be developed by experimentalists. It is critical to evaluate further the models with regard to oxidant field and to aerosol composition and properties simulations. In parallel to supporting experimental work, current model development could focus on:

* simulation of size dependence of aerosol composition and properties;

- parameterization of heterogeneous reactions and of multiphase chemistry and their involvement in particulate organic mass formation; and
- expansion of the current representation of SOA formation in atmospheric models (volatility controlled gas-to-particle partitioning into a liquid organic aerosol phase) towards solubility-volatility-reactivity controlled partitioning of aqueous/organic multiphase systems.

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6. Conclusions and recommendations

6.1. Emissions of VOC

General Conclusions

Uncertainties in VOC emissions

The huge uncertainties in VOC emissions, particularly biogenic VOC and OVOC, need to be addressed and current accuracy and precision of emission inventories need to be drastically improved.

Characterisation of VOC emissions

Adequate characterization of VOC emission variability (diurnal, weekend, seasonal, *etc.*) was identified as being crucial to our understanding of current and future emissions. New and existing platforms are required to make high quality science-based (rather than policy-based) long-term measurements.

Analytical techniques

New analytical techniques need to be developed, refined, and widely deployed to measure concentrations and fluxes of VOC, especially OVOC, long-chain VOC, and reactive BVOC.

Submission of valid data

Data discipline on the part of scientists needs to be encouraged and better access to VOC emissions data needs to be facilitated.

Impact of global change

Predicting the effects of global climate change factors (such as increases in ambient CO_2, O_3, ambient temperature and response to droughts and flooding) on BVOC emissions is highly uncertain and requires an improved understanding of the biochemistry and physiology of emissions, including updating “Guenther’s algorithm”. This should be an extremely high priority for future investigation.

Specific recommendations for improving emission estimates for VOC

Priorities for anthropogenic VOC and OVOC

* Characterise the sources, fluxes and variability (diurnal, weekend, seasonal, climate, *etc.*) of VOC, especially OVOC and long chain compounds. The seasonal variation of solvent evaporative emissions in particular needs to be better characterized.

* Continue to develop, refine and widely deploy new analytical techniques for measuring concentrations and fluxes of VOC, especially OVOC.

* Make measurements to compare as many different cities as possible to establish city “ecotypes”, especially for cities in poorly-studied regions.

* Employ isotope studies to distinguish between anthropogenic and biogenic VOC sources, especially for OVOC.

Priorities for biogenic VOC

* The huge uncertainties in VOC emissions need to continue to be addressed. Current emission inventories need to be drastically improved.

* Many more compounds need to be considered and there is a need to include all major plant species.

* Primary emission measurements at branch or leaf level are needed under conditions where fast oxidation reactions of released reactive VOC species are excluded.

Biogenic VOC responses to climate change

* Long-term year-round VOC flux measurements are needed, especially for tropical ecosystems for better understanding of current emissions, and to monitor future changes.

* Light and temperature alone only are not sufficient to predict the response of emissions to global change. There is a need to include seasonality, ecophysiology, water availability, etc. Circadian controls may also be important for how plants react to change.

Improving VOC within models

* Better speciation of AVOC by compounds and emission category is needed, together with more OVOC species. Algorithms should be included for BVOC.

* Emission measurements are needed where there are large data gaps – *e.g.* tropical forest, Africa, South America. Funding will be required.

* There is a need to support primary emission measurements at a plant species level.

* Quality-controlled measurement data should be made available and submitted at the time of publication. Such data need to be submitted to a recognised archive in standard format to be widely accessible for use in models.

* Journals should be encouraged to mandate that references to data files, secured in a recognised archive, accompany any articles that are published.

* There is a need to secure long term resources to maintain a living, expert-validated emission inventory.

* Methodology for model comparisons requires better overlap of species in model emission inventories.

Recommendations for future satellite work

* Continue gathering data and adding measurement capability, for both satellite and terrestrial platforms.

* There is a need for higher spatial and temporal resolution satellite measurements.

* Geostationary satellite instruments are needed to capture and account for large diurnal trends in many measured compounds.

* More emphasis should be made on limb measurements because of their better vertical resolution.

* Improvements are needed in the knowledge of basic laboratory spectroscopy to underpin the spectroscopic determination of VOC.

QA/QC recommendations

* All VOC measurements reported to archives should be accompanied by appropriate supporting sampling protocol information.

* Good QA/QC protocols, for both AVOC and BVOC, need to be supported, including inter-comparisons where possible.

* There is a need to encourage the development of new technology to improve techniques to make and share standards.

Long-term measurements

- Existing long term measurement platforms should continue to be supported, the scope of VOC measured should be extended, and new, carefully selected, measurement sites in strategic remote, rural and urban locations added. New measurement techniques should be included as they become available.
- Satellite measurements should be developed and used to extend the scale of measurement stations.
- Priority species should be defined – including satellite products and global change compounds. One could build on recommendations for specific gases to measure from recent WMO/GAW workshop. Glyoxal and supporting tracers such as CO, methyl bromide and other halogenated VOC should be added to the list where possible.
- New modelling tool, such as particle dispersion models, should be further developed and employed to interpret measurement data in terms of changing emissions. Back trajectories, by themselves are insufficient,

6.2. Uncertainties in local, regional and global processing of VOC

General recommendations

VOC and SOA: similarity in origin and treatment

The group recognised that, in trying to understand the atmospheric degradation of VOC, it is unrealistic to separate chemical processes generating oxidants (*e.g.* ozone, nitrates) from those which lead to the formation of SOA, since both are products of the same chemical processes.

Simplification of mechanisms

It was also recognised that the representation of such processes in the majority of atmospheric models needs to be substantially simplified. However it is essential to establish a sound methodology which allows fundamental information from laboratory and theoretical studies of elementary reactions to feed through to appropriate reduced mechanisms.

Availability of VOC kinetic information

Kinetic and mechanistic information related to the atmospheric oxidation of VOC are continuously being produced. Although some of the most important kinetic data is recorded in evaluated databases (*e.g.* IUPAC sub-committee on gas kinetics), the reactions of many VOC are not included at all. The group recommended that a new community-wide approach is required to produce a comprehensive current database of all relevant kinetic and mechanistic information. This needs to be coordinated on an international level and may require the assistance of publishers, as in other scientific areas, to ensure that reported data are inserted into a database at the time of publication.

Principal uncertainties

- The variation in VOC oxidation product distributions as a function of temperature and also at low NOx concentrations
- Kinetics and mechanisms for the reactions of NO_3 with multifunctional unsaturated hydrocarbons and large biogenic compounds.
- Mechanistic information for key anthropogenic compounds (aromatics and alkanes > C_5).

* Kinetics and mechanisms for the atmospheric degradation of nitrates, hydroperoxides and multifunctional organics.

* The reactivity of oxygenated and multifunctional peroxy and oxy radicals.

* The range of NO_3 concentrations in the atmosphere and hence its importance as an oxidizing species for VOC.

* The emissions of VOC from terrestrial biogenic and oceanic sources.

Future research activities

* Laboratory kinetic and product studies on VOC and their radical intermediates that make full use of new and emerging analytical techniques.

* The continued use of theoretical approaches to probe reaction mechanisms and provide estimates of parameters such as vapour pressure and Henry's Law constants.

* The continued development of detailed chemical mechanisms that evolve with advances in our knowledge of VOC chemistry. Subsequent testing of the mechanisms against data obtained from chamber and field studies.

* Comparison of field observations, including satellite data, with predictions based on laboratory data and models.

6.3. Production, properties, and removal of SOA

Secondary organic aerosol provides the greatest challenge at the current time, both conceptually and experimentally: in the absence of clear characterisation of the species involved and the problems associated with measurements of the composition and properties of the aerosol, it is very difficult to formulate the necessary components required to model SOA adequately. Group 3 listed several key questions with regard to SOA in the troposphere.

* What are the most important precursor VOC for SOA? Are all important SOA precursors identified and taken into account? Are chamber experiments appropriate for ambient air simulations?

* Which processes are most relevant for SOA formation (*i.e.* nucleation, condensation, cloud processing, heterogeneous and multiphase chemical processing)?

* Which processes are most relevant for SOA removal (*i.e.* dry deposition, wet deposition, SOA volatilisation)?

In addition the group pointed out the appreciable shortcomings in model predictions for SOA in the real atmosphere. It was clear that updated parameterizations of SOA formation in models needed

Field work

The group recommended that future experimental work should focus on the following.

* Field experiments to test predictions of SOA from biogenic VOC in polluted and clean environments.

* Identification of truly representative SOA precursors from anthropogenic and biogenic sources.

* Laboratory studies to test gas-phase mechanisms of VOC oxidation and multiphase chemistry, particularly with regard to the formation and partitioning of

molecular building blocks for SOA, such as small acids, dicarboxylic acids, hydroperoxides, unsaturated aldehydes, glyoxal.

- Development of instrumentation to improve the sensitivity of analytical techniques to detect the low concentrations and more complex molecules in real atmospheric aerosol at a molecular level.
- Studies of the optical, chemical and hygroscopic properties of SOA, and of SOA yields under low NO_x and low VOC precursor concentrations. Attempts should be made to answer the question: can the concentration dependence observed for α-pinene be generalized to other VOC?

Modelling

Future modelling efforts to test novel ideas that need to be developed by experimentalists would be helpful. It is critical to evaluate further the models with regard to oxidant field and to aerosol composition and properties simulations. In parallel to supporting experimental work, current model development could focus on the following.

- Simulation of size dependence of aerosol composition and properties
- Parameterization of heterogeneous reactions and of multiphase chemistry and their involvement in particulate organic mass formation
- Expansion of the current representation of SOA formation in atmospheric models (volatility controlled gas-to-particle partitioning into a liquid organic aerosol phase) towards solubility-volatility-reactivity controlled partitioning of aqueous/organic multiphase systems.

7. Thanks

The editors of this AVOC report would like to thank, in particular, the Rapporteurs who bore the burden of ensuring that the meeting was correctly reported, as such were the prime architects of its success. We would also like to thank the plenary speakers who each provided an excellent overview and set the scene for the discussion, and the Chairs who highlighted the issues and ensured that there was a fair and open discussion. And also the participants for their lively presentations and thoughtful contributions to all the issues discussed.

All our thanks are also due to ACCENT for providing the funds to facilitate such meetings, and to the staff of the Barnsdale Hall Hotel for providing the facilities and help which made this meeting an undoubted success.

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

8. Plenary Lectures

Emission of Biogenic Volatile Organic Compounds from Vegetation: Volatile Isoprenoids

Plenary Lecture to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Plants emit in the atmosphere volatile hydrocarbons of different metabolic origin. Volatile isoprenoids (isoprene and monoterpenes) are emitted in large quantities and at a very large metabolic cost for plants. They also influence the chemistry of the troposphere. In perturbed environments with substantial loads of anthropogenic compounds, volatile isoprenoids can power the formation of ozone, photochemical smog, and particulate. Crucial to improve models and algorithms of isoprenoid emission and to predict their contribution to chemical reaction in the atmosphere, is the knowledge of the biochemical and ecological bases of isoprenoid formation. It is shown how interdisciplinary studies have driven to a) the preparation of detailed inventories of isoprenoid emitters, b) the discovery of a novel biochemical pathway from which volatile isoprenoids are formed, c) the understanding of environmental control on isoprenoid biosynthesis and emission, in turn leading to the preparation of an emission algorithm based on the response to light and temperature, d) the comprehension of functional roles of isoprenoids in plants. It is suggested that these new scientific finding could lead to improved models for predicting isoprenoid emission and their impact on biosphere-atmosphere interactions.

Introduction

Plants exchange with the atmosphere a large number of volatile organic compounds (VOCs), some of which have very important roles both in plant defence and in the chemistry of the troposphere. This review focuses on volatile isoprenoids, compounds that are emitted at very large rates by many plant families. Volatile isoprenoids are isoprene (2 methyl – 1,3 butadiene) and monoterpenes. Isoprene is the most abundant non methane hydrocarbon in the atmosphere with emissions from plants currently estimated at at least 500 Tg C y^{-1} [Guenther *et al.* 1995; Fuentes *et al.* 2000], about half of the total emission of biogenic hydrocarbons. Monoterpene emission is estimated to be lower than isoprene emission, but year round emission measurements with accurate instrumentation are now making necessary a continuous revision of the estimation of monoterpene measurements.

Isoprenoids are very reactive and this is the reason why they are so important in atmospheric chemistry. Photochemical reaction time constants of isoprenoids with ubiquitous OH radicals vary between minutes and hours [Brasseur and Chatfield 1991] and the products of these reactions may have very different fates. In a perturbed atmosphere with considerable load of atmospheric pollutants, especially NO, oxyradicals and aldehyds formed by isoprenoids and OH· may enhance the yield of NOx contributing to ozone formation [Fuentes *et al.* 2000]. The cycle is autocatalytic as ozone may again form photochemically OH. These photochemical reactions were found to generate ozone episodes around large cities [Chameides *et al.* 1989], although the ozone production depends on the ratio between VOCs and NOx, being optimal for ratios between 4 and 15 [Finlayson Pitts and Pitts, 1999]. Some isoprenoids are also involved in the formation of particulate [Kavouras *et al.* 1998] and aerosols [Griffin *et al.* 1999], which are now among the most dangerous pollutants in urban areas. Finally, isoprenoids may indirectly favour the accumulation of less reactive greenhouse gases, such as methane, successfully competing for OH· with these compounds [Brasseur *et al.* 1991].

For the above given general reasons, there has been considerable and converging interest over the years between atmospheric chemists, environmentalists and plant biologists to study the biogenic emissions of isoprenoids. Stepping from this interest, a number of multidisciplinary projects were and are internationally funded. At the European level, the pioneering efforts of projects such as the EC supported BEMA (Biogenic emission in the Mediterranean Area, see BEMA special issue, 1997), have built excellence in European research. Currently the network of excellence ACCENT, the Marie Curie research and training network ISONET and the European Science Foundation programme VOCBAS address fundamental questions to further increase our knowledge about biogenic isoprenoid emissions and their effects on the environment. We will briefly try to summarize the work done up to now, and the current perceptions about the following four questions: a) which plants emit isoprenoids; b) how are isoprenoids formed; c) how the environment controls isoprenoids; and d) which are isoprenoids functions in plants.

Isoprenoid emissions by plants: inventories and evolutionary considerations.

Since Went’s perception that plants emit hydrocarbons able to form photochemical smog [Went 1960] plat biologists have carried out inventories to determine which plants could be responsible for these emissions. This is the most important information to be able to map the emission at a global scale. Yet, in 1991 Fall wrote that “ .the published screening for isoprene emitters include….only approximately 140 plant species of an estimated 240.000 living species…” [Fall 1991], calling for more extensive contributions in the field of emission inventories.

In fact several inventories have been recently published. The comprehensive paper by Kesselmeier and Staudt [1999] reports emissions of isoprenoids and oxygenated VOCs from a large number of species, especially boreal but also exotic. The emission from austral vegetation is also investigated, especially under the frame of international research programmes such as Expresso in the African savannahs, and LBA in the Amazon. The use of internet to post inventories of isoprenoid emission was first exploited by Hewitt and coworkers in the Lancaster group and this site (http://www.es.lancs.ac.uk/cnhgroup/iso-emissions.pdf) is still a very useful source of information for people interested in emission inventories. More recently, the task of inventorying isoprenoid emissions has been included in the Global Emission Inventory Activity (GEIA). This inventory has been developed in collaboration with the ACCENT network of excellence, and has taken on board the emission inventory by the National Centre for Atmospheric Research of USA (NCAR). The GEIA-ACCENT inventory under the supervision of Alex Guenther is now available at http://www.geiacenter.org/presentData/nvoc.html or http://www.aero.jussieu.fr/projet/ACCENT/database.php and offers a very complete data-set for modellers although it is weak in the species-specific discrimination of emitters.

All inventories have shown that isoprene emission is common in natural vegetation but not in cultivated plant species. The two main ecosystems emitting isoprene to a very large extent are natural forests and aquatic vegetation. Another generalization coming from inventory information is that the trait was probably lost during plant evolution, being isoprene emitters often found in lower plants such as Briophytes [Hanson *et al.* 1999] and Pteridophytes [Sharkey and Yeh 2001] and never in recently evolved taxa of higher plants such as in CAM and C4 angiosperms. Whether the disappearance of the isoprene emission trait in higher plants was driven by anthropic selection or is only attributable to natural causes is unknown.

The information about monoterpenes is not as clear as for isoprene. Monoterpene emission seems to be widespread in Mediterranean climate and is particularly strong in a few oak species [Loreto 2002]. However, it is becoming clear that many other plant species can emit large amount of isoprenoids, especially during brief period of the year. A seasonal, strong emission of trans-beta-ocimene has been reported in pines [Staudt *et al.* 2000] and other plants of the Fagales group [Schuh *et al.* 1997]. Moreover, a large group of plants have evolved the capacity to store monoterpenes in specialized organs, either ducts or glands. These plants are generally weak emitters but the emission can be massive when reservoirs are broken [Alessio *et a*l. 2004]. This often occurs in nature as a consequence of mechanical stresses of biotic or abiotic origin. The influence of human selection on this class of monoterpene emitters is clear, as these compounds are used in pharmaceutics and are of importance in human alimentation. Officinal plants storing monoterpenes are therefore cultivated around the world.

Despite the fact that some general schemes are now being delineated about isoprenoid emitters, there are important reasons to continue to carry out inventories of isoprenoid emissions. First, we are still in demand of measurements in remote areas, especially where natural emissions can interact with the movement of large and polluted air masses, *e.g.* the case of monsoon-driven Asian Brown Cloud over the Himalaya range. Second, technical developments have now made available instrumentation that can detect with unprecedented accuracy (down to ppt level) and fastness (on-line, without any preconcentration steps) isoprenoid emission. The use of Proton Transfer Reaction Mass Spectrometry can for instance reveal weak emitters and track the age and season-dependency of the emission [Lindinger *et al.* 2005]. It may also be used to up-scale measurements from single leaf to canopy level allowing very rapid flux measurements [Karl *et al.* 2001, Karl and Guenther 2004]. This will certainly be important to determine the intra-canopy reactivity of isoprenoids and other biogenic VOCs.

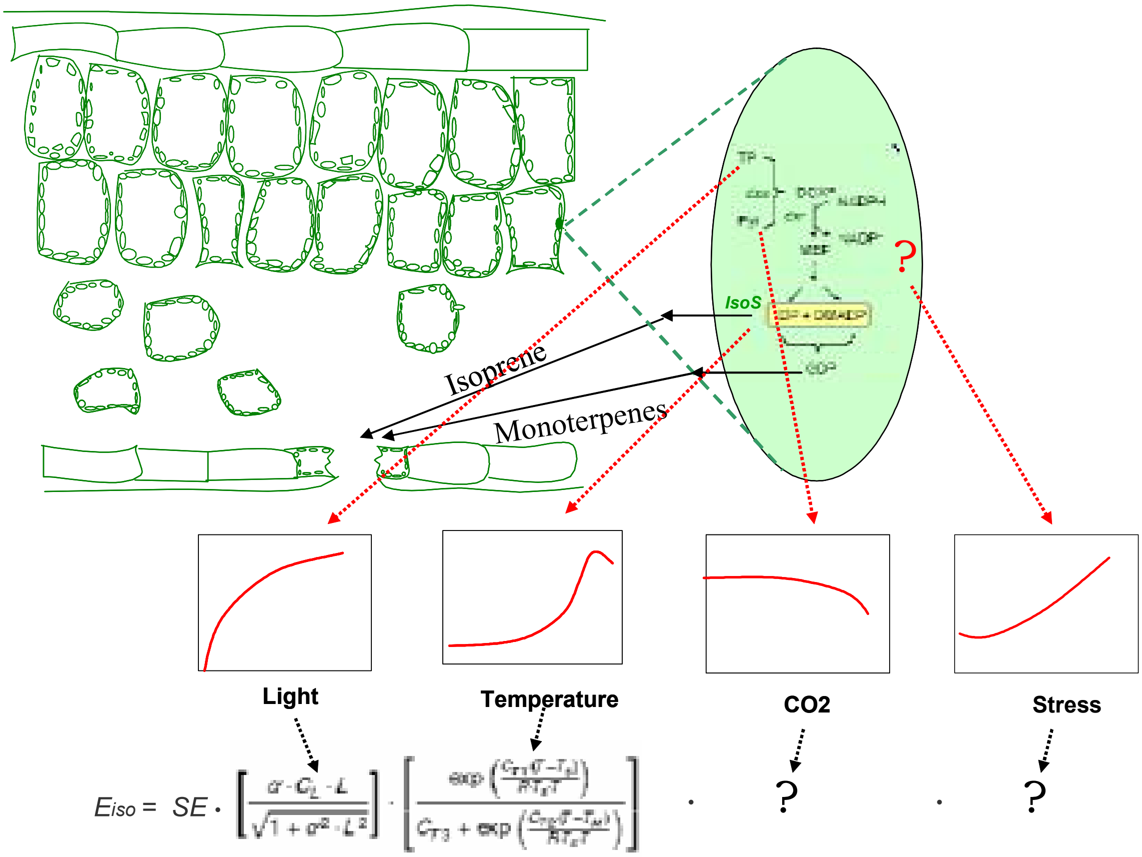
Isoprenoid formation and environmental control: algorithms of isoprenoid emission

In this section we will focus only on volatile isoprenoids that are not stored in specialized organs, as they represent the largest fraction of the emission of isoprenoids in undisturbed ecosystems. Isoprenoid emission is dependent on light. The discovery of the light-dependence of isoprene [Loreto and Sharkey 1990] and monoterpene emission [Loreto *et al.* 1996a], very similar to the light-dependence of photosynthesis, and described by a rectangular hyperbola, first set the ground for understanding the course control of photosynthesis over the synthesis of isoprenoids. The tight relationship between isoprenoid formation and photosynthesis was also unambiguously proved by the quasi-complete and fast labelling of the carbon skeleton of volatile isoprenoids [Delwiche and Sharkey 1993, Loreto *et al.* 1996b]. A novel, chloroplastic pathway, was then described on the basis of intra-molecular labelling [Lichtenthaler *et al.* 1997], and clearly distinguished from the cytosolic (mevalonic) pathway of isoprenoid formation (Figure 1). More recent studies have focussed on the regulation of the chloroplastic pathway that seems to involve both substrate and enzymatic controls. The light-dependence of isoprenoid emission reflects the light-dependence of glyceraldehyde-3-phosphate (G3P), the photosynthetic intermediate shunting into the chloroplastic pathway of isoprenoid formation, as well as the lack of chemical energy (ATP) and reducing power (NADPH).

Volatile isoprenoid are also temperature-dependent and the relationship between temperature and emission is exponential at temperatures regularly experienced by plants during the vegetative season (20-35 °C). Temperature is therefore perhaps the most important driver of isoprenoid emission. The temperature-dependence of isoprenoid emission does not reflect a similar dependence of the reaction of the photosynthetic cycle. Thus, there must have been a different control driving isoprenoid response to temperature. The Q^{10} of the process (the increase of the emission for a corresponding increase of temperature by 10 °C) is as high as 2-4, and this was thought to reflect the temperature-dependence of some enzymatic reactions. In fact, it was first discovered by Monson and coworkers [1992] that the temperature-dependence of isoprene emission reflected the temperature-dependence of isoprene synthase, the enzyme catalyzing the last reaction of the pathway, the formation of isoprene from the immediate precursor dimethyll-allyl-diphosphate (DMADP). Isoprene and monoterpene synthase activities seem to control isoprene emission in several cases, explaining for instance the seasonality [Fischbach *et al.* 2002] and the daily trend of the emission [Brueggemann and Schnitzler 2002].

The emission of volatile isoprenoids seems to be insensitive to variations (small increases) of CO_2. This is again a very important finding since it uncouples the process of isoprenoid synthesis from its main driver, photosynthesis. It also shows that isoprenoid emission may not increase in response to future CO_2 levels in the atmosphere, although the simultaneous increment of temperature [IPCC 2001] can overall bring to an increase of biogenic isoprenoid load in the atmosphere. Several researches have shown that very large increments of CO_2 concentration (generally more than double the ambient concentration) can surprisingly inhibit isoprenoid formation [Scholefield *et al.* 2004, Rosenstiel *et al.* 2004]. There may be several reasons for this, but the most likely explanation is considered at the moment the onset of a strong competition of respiratory processes for pyruvate, the carbon source of isoprenoids shuttling into the chloroplasts to merge with G3P, the photosynthetic source [Rosenstiel *et al.* 2004].

The environmental control of isoprenoid emission is very predictable and this has made possible the elaboration of a very useful and simple algorithm for predicting the emissions at leaf level [Guenther *et al.* 1991, Guenther *et al.* 1995, Guenther 1999]. In its simplest elaboration, the algorithm is based on the light and temperature dependence of isoprenoid emission, applying two correction factors to a standard emission, that is the emission measured at standard temperature and light intensity (Figure 1). However, as above already noted, there are numerous physiological and environmental factors controlling the standard emission. It is now urgent to improve the algorithm to incorporate these findings, especially when the factors controlling the emission are easy to model, as is the case for the leaf age and the impact of season. Modelling isoprenoid emission on the basis of plant physiology rather then on the basis of empirical environmental factors, would be preferable but is a challenging task, because of the large number of drivers and constraints. The two models currently published, the SIM-BIM model [Zimmer *et al.* 2000] and the model based on photochemical electron transport [Niinemets *et al.* 2002] are biased by a degree of complexity that makes them scarcely useful for practical applications.



$$E_{iso} = SE \cdot \left[\frac{\alpha \cdot C_L \cdot L}{\sqrt{1+\alpha^2 \cdot L^2}}\right] \cdot \left[\frac{\exp\left(\frac{C_{T1}(T-T_S)}{RT_S T}\right)}{C_{T3}+\exp\left(\frac{C_{T2}(T-T_M)}{RT_S T}\right)}\right] \cdot ? \cdot ?$$

Figure 1. Volatile isoprenoids are formed in chloroplasts from a dedicated biochemical pathway. In black are shown key substrates of the pathway: triosophosphate (TP), pyruvate, deoxyxylulose-5-phosphate (DOXP), methylerythritol phosphate (MEP), isopentenyl diphosphate (IDP) and its isomer dimethylallyl diphosphate (DMAPP), an geranyl diphosphate (GDP). In green are shown key enzymes for isoprenoid biosynthesis, deoxyxylulose-5-phosphate synthase (DXS), deoxyxylulose-5-phosphate reductoisomerase (DXR), and isoprene synthase (IsoS). Red arrows show the limiting steps influenced by environmental conditions: light, temperature, CO_2, and environmental stress (unidentified and therefore marked as ?). The four panels describe the response of the emission to each one of these four factors. Below each panel is the elaboration which describes mathematically the response and is incorporated in the algorithm predicting emissions on the basis of environmental factors. The influence of CO_2 and stresses have been experimentally described but have not been yet included in the algorithm. In the algorithm, based on Guenther *et al.* [1991, 1995, 1999], Cl, α, Ct1, Ct2, Ct3 and TM are empirical coefficients, L is the photosynthetic active radiation, Eiso is the actual isoprenoid emission, SE is the standard emission rate, R is the universal gas constant, T is the leaf temperature, and Ts is the leaf temperature at standard condition =303 °K.

Isoprenoid functions in plants

The ecological question why plants emit isoprenoids is also relevant, as a considerable part of the carbon fixed by photosynthesis can be invested by leaves in isoprenoids (and lost to the atmosphere). It has been observed that isoprenoid synthesis persists in drought-stressed leaves [Sharkey and Loreto 1993] and may even be stimulated in response to stresses, such as in leaves recovering from drought [Sharkey and Loreto 1993] and after exposure to ozone [Loreto *et al.* 2004]. The investment of carbon into isoprenoids may exceed the availability of carbon fixed by photosynthesis, which indicated that alternative carbon sources can be used, when needed, to form isoprenoids

[Schnitzler *et al.* 2004]. All these evidences support the idea that isoprenoids have a very relevant functional role in plants.

Sharkey and Singsaas [1995] first showed that isoprene is involved in a mechanism of thermal protection, as leaves emitting isoprene were able to withstand higher temperatures. Loreto *et al.* [2001] broaden this perspective, maintaining that volatile isoprenoids have a more general defensive action against all oxidative stresses, including drought, high temperatures and exposure to gaseous oxidative pollutants. There has been no clear consensus in the scientific community about these findings. Even more controversial is the mechanism by which volatile isoprenoids exert their putative protective action. There is the possibility that the lipophylic isoprenoids interact with lipids in membranes strengthening membranes exposed to stress [Sharkey and Yeh 2001] but isoprenoids may also react in the intercellular spaces (and even in the leaf boundary layer) with toxic reactive oxygen species, decreasing their pressure over membranes, and the consequent damage. A very recent report has shown that isoprene may interact with NO formed in stressed leaves and responsible for the starting of the signalling cascade which leads to programmed cellular death. This very important modulating action may explain why isoprene reduces the ozone visible damage in leaves [Velikova *et al.* 2005]. Monoterpenes are also very active molecules against biotic stress [Pare' and Tumlison 1997]. They may efficiently deter insect and herbivore feeding and block the colonization of wounding by bacteria and fungi.

Irrespective of the mechanism, it seems clear that stresses may dramatically influence the emission of isoprenoids. Plants are continuously exposed to environmental constraints in nature, and an attempt should be made to incorporate the information from stress physiology into a revised algorithm of isoprenoid emission, in order to improve the predictability of models (Figure 1).

Conclusions

The large and interdisciplinary community of scientists studying isoprenoid emission by plants has provided remarkable insights into biosynthetic mechanisms, functional roles, environmental control, and fate in the atmosphere of the emitted compounds. More challenging studies have been or should be undertaken to increase our understanding of the metabolic and environmental control over the emission and to improve current emission models. Predicting isoprenoid emission in the atmosphere may be crucial in a rapidly changing environment, both for the survival of plants in extreme environments and for the understanding and control of pollution episodes powered by biosphere-atmosphere interactions.

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Where are the Major Uncertainties in Atmospheric VOC Chemistry?

Plenary Lecture to the ACCENT Workshop on Volatile Organic Compounds: Group 2

Jonathan Williams

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Douglas Adams: *"We demand rigidly defined areas of doubt and uncertainty!"*

The uncertainty in our knowledge of organic trace gases will be examined under four sections: 1) emissions, 2) chemistry, 3) upper troposphere, and 4) the future

1. Emissions

In several cases where models have been compared with measurements a trend is followed but the absolute numbers are off, by as much as a factor of 3 in the case of the MPI-MATCH model.

Uncertainty can be assessed by examining different emissions assessments.

For anthropogenic inventories we have RETRO, IIASA and EDGAR. While all three inventories have *circa* the same total emissions, the apportionments differ significantly, *e.g.* between domestic, traffic and industrial sources.

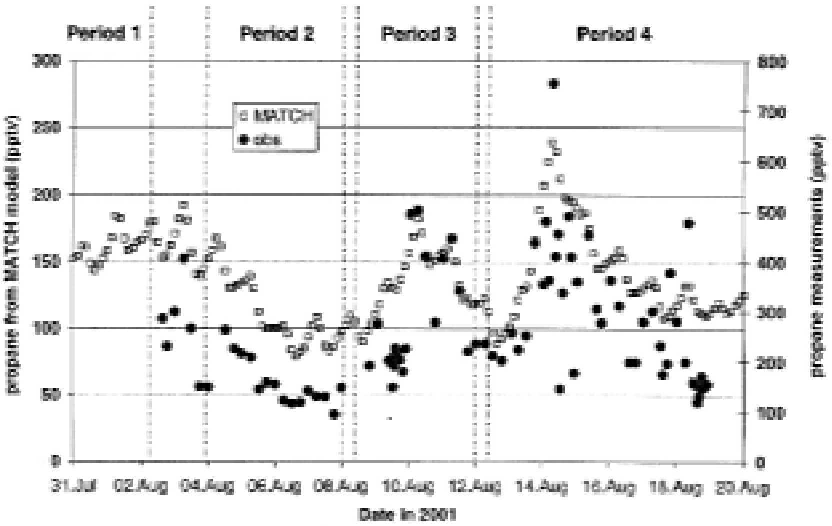


Figure 1. Comparison of modelled and measured values for propane in the lower troposphere

Uncertainty in emissions inventories is being reduced by global networks of measurement. This eliminates the need for large extrapolations. Example, Detlev Helmig and the NOAA canister network for alkanes.

Biogenic emissions are thought to be at least 10 times greater than anthropogenic. However, there is considerable disagreement between models and measurements at the interface between vegetation and atmosphere. In particular the models find that isoprene emissions which are scaled up from the leaf scale are too high to maintain an OH. Thus isoprene is very different in the model and measurements.

Recently OH measurements show that OH is not depleted over the rainforest as previously thought. Bigger differences between modelled and measured OH are found at higher isoprene levels, both over the rainforest and over the eastern United States.

Recent flux measurements made over the jungle also suggest large nocturnal uptakes of VOC, which are not included in models at present.

A further surprising finding also from the rainforest related to biogenic emissions was that the Tropical jungle seems to emit preferentially more alpha-pinene. This is currently not explained.

The ocean has been identified as an area of considerable uncertainty for VOC. Despite its size and potential importance the ocean is poorly understood in terms of VOC emissions and uptake. The example of acetone is given, for which budget estimates did not include the ocean until 2002. In this paper the ocean was thought to be a source of acetone although measurements suggest it is a sink globally, but a source where light and biology are present. Recent work from ships and from mesocosms supports this theory.

Biomass burning is inherently uncertain, being a factor of a myriad parameters, moisture, type of fuel, type of burn, *etc*

Finally in this section it is noted that we can expect uncertainty and surprises wherever we measure, at least based on past experience. Numerous examples of recent findings are given, for example, methane emissions from plants, methyl chloroform emissions from Europe, methyl iodide emissions with dust and seawater.

2. Chemistry

The chemistry of the atmosphere is uncertain judging by the current large disagreement between models and measurements. An example from the ICART experiments is given.

Formaldehyde is a good indicator of our current understanding. In the quiescent mid troposphere we can model formaldehyde reasonably well. However, close to sources or in the upper troposphere, or in the outflow of convection we can be up to a factor of 5 out. This is important since formaldehyde is an important step in HO_x production.

In the lab there have been many measurements of OH + VOC. While generally the initial rates are well known, the products and their dependence on temperature and pressure are less certain. Also uncertain are photolysis cross sections and quantum yields (and their temperature dependences).

Again using the example of acetone, we note that the lifetime of acetone has been recently reassessed and is now considered to be much longer lived than previously thought.

Finally in this section, recent total reactivity measurements made in the field indicate that we are not measuring all the important VOC in the atmosphere. That is to say there is a large difference between the measured total reactivity and the sum of the individual components.

3. Upper troposphere

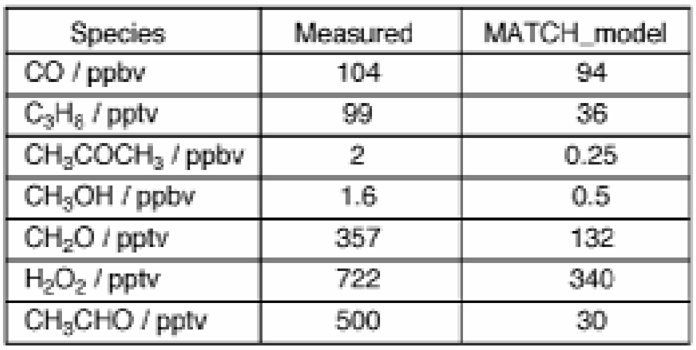
Using model measurement comparisons as a gauge of uncertainty, we see particularly poor agreement in the upper troposphere. Comparisons of measurement of MATCH with measurements in UTOPIHAN AT are particularly striking. Likewise recent comparisons of peracetic acid show poor agreement in the upper troposphere.

One big problem is acetaldehyde. It is very important to measure and yet there is evidence of artefacts in all systems to date. Interferences from ozone and changing humidity seem to be important factor here.

We note again how drastically the acetone lifetime has changed recently and point out that now the PAN budget has little influence from acetone if there is only a few hundred ppt of acetaldehyde.

Finally the biggest uncertainty in the upper troposphere comes in the vicinity of convection. Inexplicable high amounts of H_2O_2 and methanol emerge from cloud outflows and models find it difficult to reproduce formaldehyde production rates in these situations.

Table 1. Comparison of measured and modelled values for selected VOC in the upper troposphere between 8 and 12 km.



Species	Measured	MATCH_model
CO / ppbv	104	94
C_3H_8 / pptv	99	36
CH_3COCH_3 / ppbv	2	0.25
CH_3OH / ppbv	1.6	0.5
CH_2O / pptv	357	132
H_2O_2 / pptv	722	340
CH_3CHO / pptv	500	30

New data is emerging on hydroperoxides but since this is dangerous work little has been done so far. Furthermore interaction of VOC with ice surfaces and clouds is still in its infancy and therefore uncertain.

4. The future

It is predicted that temperature, CO_2 and ozone will increase.

1) How will the biosphere (the strongest VOC emitter) respond?
    - Ocean pH and temperature may lead to different phytoplankton/emissions.
    - Emissions increase/decrease, faster growth?
    - Land use changes – desertification, deforestation.
    - Atmospheric circulation changes / hydrological cycle changes?
    - Ozone affects the lifetime of signalling compounds.
    - At high NOx, isoprene emission not a good plant strategy?
2) Future energy choices
    - If oil and gas get expensive what then? (coal/nuclear/renewables/fusion)
    - Hydrogen economy?
3) Satellites – Can they reduce VOC uncertainty?
    - HCHO
    - PAN, acetylene, ethane, CFC 11, CFC 12, methylglyoxal

  - Burning locations, area and volume

4) What is the VOC impact of current Geoengineering proposals?

  - Crutzen - 1-2 Tg injections of sulfur or black carbon.
  - Iron Fertilisation of the Ocean.
  - Intensive monoculture tree planting.

5 Summary

1. Emissions Uncertainty;
   <u>Oceanic</u> >> Terrestrial <u>Biogenic</u> >> Pyrogenic > Anthropogenic.
2. Chemistry, OH + VOC → well known for rate but not for products, particularly at low T and NOx.
3. Photolysis rates and potential effects of HO_2 at low T needs more investigation.
4. We need to measure acetaldehyde and Cy accurately.
5. Atmospheric interface regions/interactions uncertain
   – ice, dust, sea, jungle, UT.
6. Acetone – sources and sinks still uncertain?
7. Biological response to climate changes; uncertain for VOC.
8. Future issues – There are many future issues for VOC specialists to consider.

In conclusion:

R.I Fitzhenry: *Uncertainty and mystery are energies of life. Don't let them scare you unduly, for they keep boredom at bay and spark creativity.*

Modelling Carbonaceous Aerosol over Europe: Recent Results and Status

Plenary lecture to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Introduction

Particulate carbonaceous matter (PCM) is believed to contribute to around 30 % of PM levels at rural and natural background sites in Europe [Putaud *et al.,* 2004]. Understanding of the sources of PCM is severely limited though. The chemical composition is largely unknown, with less than 20 % typically identifiable using GC/MS methods [*e.g.* Turpin *et al.*, 2000]. There have been very few direct measurements which allow a determination of how much of PCM is from anthropogenic versus biogenic sources, or from primary emissions versus from secondary organic aerosol (SOA) formation. Recent reviews have highlighted the complexity of carbonaceous aerosol both in terms of known composition and formation mechanisms [Fuzzi *et al.,* 2006; Kanakidou *et al.,* 2005].

However, over the last few years some measurement results have become available which have started to shed light on the important sources of PCM in Europe. For example, Szidat *et al.* [2006] used ^{14}C-analysis to attribute the sources of aerosol in Zurich, Switzerland to either 'fossil' carbon (from coal, oil) or 'modern' carbon (from recent vegetation, either by combustion or emissions). They found that fossil-fuel combustion accounts for *ca.* 30 % of OC throughout the year, even in the city centre. Biomass burning in wintertime and SOA in summertime seem to account for the majority of the remaining OC. Using a network of Nordic sites measuring number distributions, combined with extensive trajectory analysis, Tunved *et al.* [2006] has shown a very good relationship between accumulated terpene emissions and particle mass changes, suggesting that in clean-air conditions at least the build-up of PM can be interpreted almost entirely in terms of biogenic precursors.

EMEP EC/OC and CARBOSOL campaigns

During 2002-2004 two measurement campaigns were conducted in Europe, in order to provide a better characterisation and understanding of PCM. The EMEP EC/OC campaign measured EC, OC, TC and PM at 15 sites, and many of these sites have complementary measurements of other species. In addition, some of the samples from the EMEP campaign have been analysed for levoglucosan. Details of the EMEP EC/OC campaign can be found in Yttri and Kahnert [2004] and Yttri and Facchini, [2005].

The EU CARBOSOL Project combined weekly measurements of EC, OC, inorganic ions, elemental composition, levoglucosan and radioactive tracers across a network of 6 sites in southern-central Europe. Further details of the CARBOSOL campaign can be found in Legrand and Puxbaum [2007]; Pio *et al.* [2007] and references cited therein.

One of the main features of the CARBOSOL project was the sampling of many tracer species. Levoglucosan was used as a tracer of organic carbon from biomass-burning (OC_{bb}), BC as a tracer (albeit crude) of primary OC emissions from fossil-fuel. Measurements of cellulose were used to determine the contribution of primary biogenic sources. Pooled filter-samples from summer and winter periods were also analysed for ^{14}C, in order to determine the percentage of modern carbon versus C from fossil-fuel sources. Gelencsér *et al.* [2007] combined all of these sources of information in an effort to calculate the relative contributions of the primary sources of C, and of the secondary sources, denoted SOA_{nf} (SOA from non-fossil fuel sources, which included condensation of SVOC from biomass-burning as well as BSOA as used here) and SOA_{ff} (SOA from fossil-fuel sources, equivalent to ASOA as used here). Each step of this analysis, *e.g.* to estimate OC_{bb} from levoglucosan, is of course very uncertain, so Gelencsér *et al.* [2007] defined both a central best-estimate value for each factor with a plausible range of uncertainty. A form of Monte-Carlo analysis was used to explore all possible combinations of these uncertain factors. In most cases, the results turned out to be rather robust, *e.g.* that SOA_{nf} dominated TC levels at most sites in summertime, and that OC_{bb} was often a major contributor in wintertime.

Modelling

During 2005/2006 an extensive series of calculations and tests has been carried out with the EMEP photo-oxidant model, in order to investigate the consistency of current emissions and SOA schemes when compared to the results of the CARBOSOL project and to the EMEP EC/OC campaign. Details of much of this work can be found in Simpson *et al.* [2007]. The model used in this work has a number of semi-volatile organic gases which are assumed to be able to condense onto (or evaporate from) pre-existing OC using gas/particle partitioning ideas. The basic SOA schemes have been described previously by Andersson-Sköld and Simpson [2001]. Two versions of the model will be referred to here. The Kam-2 version uses the gas/particle scheme as developed by Andersson-Sköld and Simpson. The advantage of this scheme compared to others available in the literature is that it was evaluated against smog-chamber experiments covering a wide-range of conditions, with α-pinene concentrations from 900 ppb to 20 ppb, NOx from 240 ppb to 0 ppb, and temperatures from 49 °C to 11 °C. A second SOA module, Kam-2X has identical chemical reactions, but with increased partitioning coefficients, which leads to significantly great SOA formation in some areas - particularly Northern Europe (where cold temperatures encourage condensation).

We have used a new inventory for annual national BC and OC emissions developed by Kupiainen and Klimont [2006]. An important advantage of this inventory is that it includes details for a very large number of sources. In particular, we were able to extract the emissions from wood-burning sources separately, which allowed a verification against the levoglucosan measurements performed within EMEP and the CARBOSOL project. Figure 1 illustrates the emissions of EC and OM, highlighting the very significant contribution of wood-burning to annual emissions.

Results

A large number of results are presented in Simpson *et al.,* [2007], illustrating for example the dominant role of BSOA across much of Europe, but especially the Nordic countries, and detailed comparisons against data for levoglucosan and other compounds. Figure 2, gives examples of the model results for total carbon (TC = OC + EC) for sites in Sweden and Slovakia, using both the Kam2 and Kam2X SOA schemes. We compare with TC rather than OC as this is the most robust measurement, avoiding the problems of defining the OC/EC split. As well as giving an idea of model performance, these Figures (bottom row) also illustrate the importance of the different sources of TC, with BSOA and wood-burning dominant in summer and winter respectively.

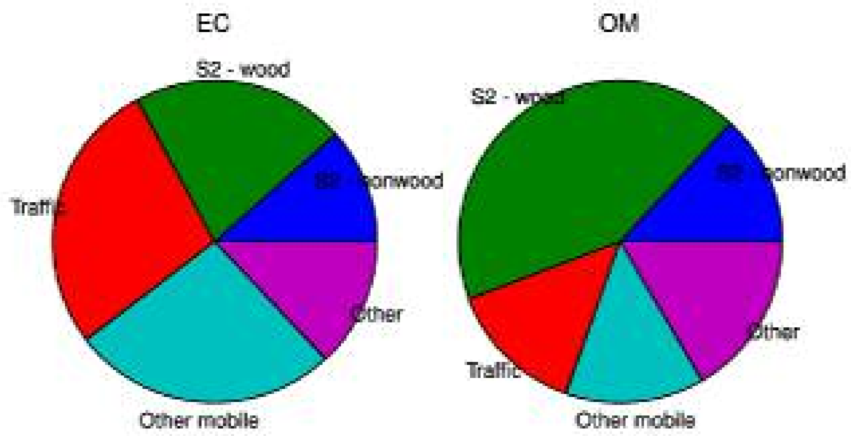
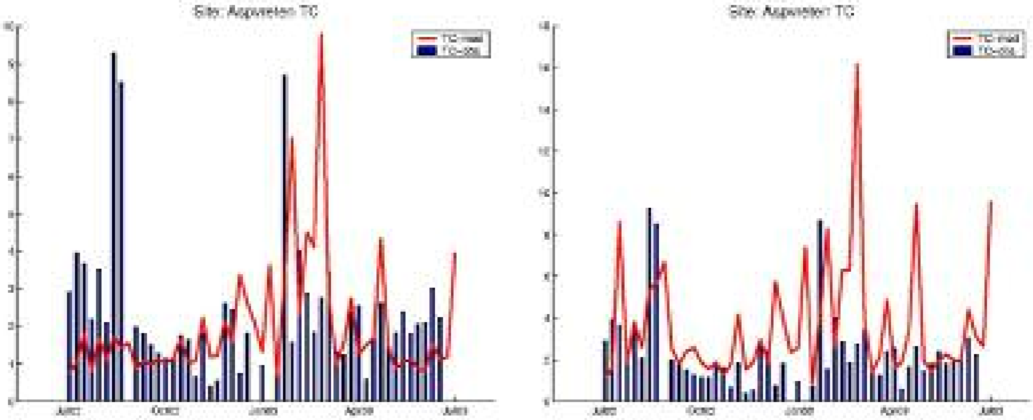


Figure 1. Emissions of sub-micron elemental carbon and organic matter in Europe, as given by Kupiainen and Klimont [2006].

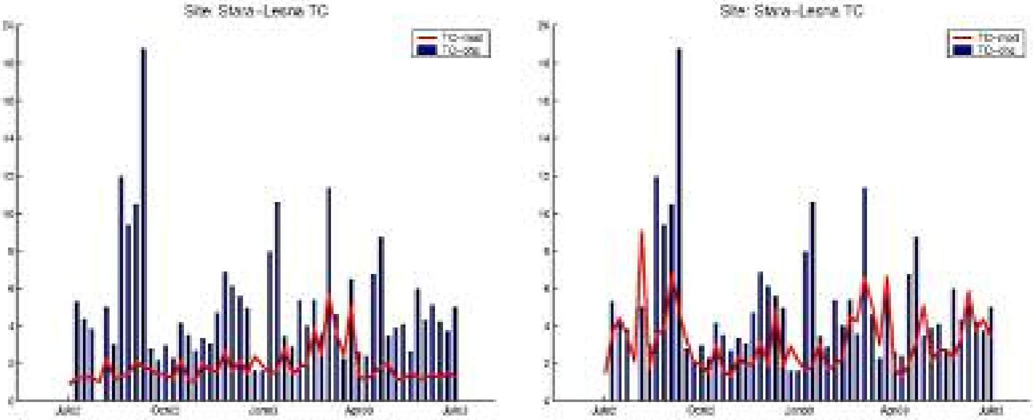
The modelling work presented in Simpson *et al.* [2007] confirms that the EMEP model does a good job of reproducing concentrations of pollutants with well-know emissions and chemistry, for example of sulphate. Further, in northern Europe the model predicts TC levels which are in line with measured values, especially with the Kam-2X scheme. These predictions are dominated by modelled BSOA. However, in southern Europe, including the CARBOSOL sites, both versions of the model significantly under-predict TC levels, especially in wintertime. Comparison with the results of Gelencsér *et al.* [2007], and with levoglucosan, suggests that the model under-predicts both the biomass burning and SOA components of the measured TC at these sites.

Table 1. Comparison of Modelled Components of Summertime TC at K-Puszta, Hungary, with Observation-derived components (5^{th}-95^{th} percentile range) from CARBOSOL data. See Gelencsér *et al.* [2007] and Simpson *et al.* [2007]for details. Units µg C m

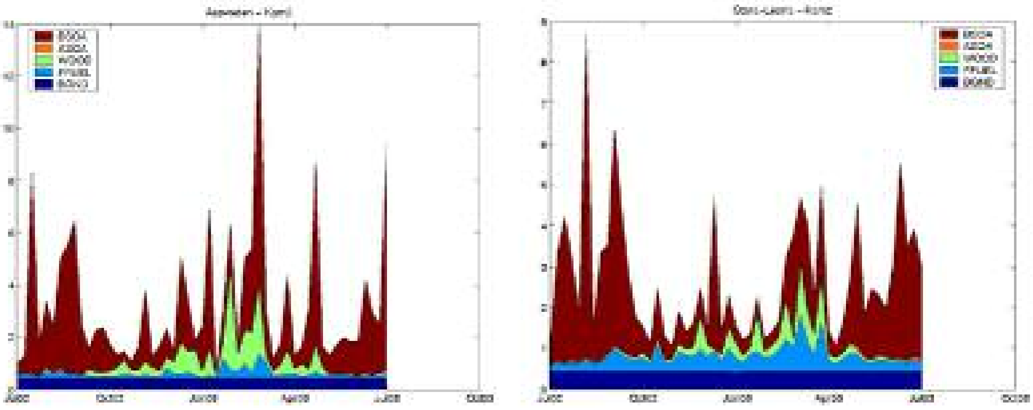
	Observed-Derived (5–95th %ile)	EMEP Model (Kam2 - Kam2X)
TC	5.2	1.6 – 2.7
WOOD	0.3 – 0.5	0.05
EC	0.4 – 0.7	0.4
FFUEL	0.2 – 0.5	0.4
BSOA	2.9 – 3.6	0.2 - 1.4
ASOA	0.05 – 0.7	0.03 - 0.04



(a) Aspvreten - Kam2 (b) Aspvreten - Kam2X



(c) Stara-Lesna - Kam2 (d) Stara-Lesna - Kam2X



(e) Aspvreten - Kam2X (f) Stara-Lesna - Kam2X

Figure 2. Modelled and Observed Total Carbon Results (ug/m^3) using two versions of the EMEP SOA model, for Aspvreten (Sweden) and Stara-Lesna (Slovakia). The bottom row shows contributions from BSOA, ASOA, Fossil-fuel (FFUEL), domestic wood burning (WOOD) and the assumed background OM (BGND)

At all sites, the contribution of BSOA far exceeds that of ASOA. The relative contribution of BSOA compared to primary organic aerosol (POA) and background components varies significantly across Europe though, and at different times of year. However, model results regarding SOA are extremely sensitive to assumptions about unknown variables. We can thus conclude that the major uncertainties associated with modelling of PCM lie with the inventories and modelling of biomass-burning emissions, and with SOA modelling.

Discussion

A large number of factors make it difficult to conduct a true verification of modelled versus observed concentrations for BC and OC. One major problem has always been that measurements of OC actually contain thousands of different and largely unidentified molecules, usually with no information on the proportion of primary, secondary, anthropogenic, or biogenic sources. Without such a distinction model verification will always be severely limited.

The most notable feature of the CARBOSOL comparisons was the strong under-prediction of (1) the biomass-burning components, and (2) the SOA components, especially for $SOA_{ff.}$ Unfortunately we have only been able to perform a detailed component analysis for the CARBOSOL sites, which are all situated in south-central Europe. However, we can conclude from the analysis of levoglucosan, BC and TC from the EMEP sites that different conclusions would be drawn in other parts of Europe. In particular, there is no evidence of a substantial under-prediction of wood-burning emissions at the Nordic sites. Further, the EMEP model tends to over-predict TC at these sites, suggesting that this scheme may generate too much rather than too little SOA.

The possible reasons for problems in modelling SOA, biomass-burning and other emissions are discussed in detail in Simpson *et al.* [2007], and cannot be reproduced here. However, it is clear that a major problem in the modelling of PCM is that too many steps in the calculation process are very uncertain, and there are too few constraints. With so many free variables, it is quite likely that judicious (or unscrupulous!) tuning of the various parameters can result in a model version which would fit the measurements quite well. It seems clear that much more work is needed to constrain the various steps of the PCM modelling process, including

- Evaluation of the emissions of BVOC. These emissions are crucial to any attempt to model BSOA, but still very uncertain. Given the fact that emissions validation is possible with today's measurement methods, this step alone would act significantly improve the most important input for PCM modelling
- Evaluation of the emissions of PM from anthropogenic sources. Mobile source as well as residential combustion emissions are still highly uncertain, but very amenable to near-source validation experiments.
- Evaluation of the emissions of heavy VOC from anthropogenic sources. A fraction of the non-primary TC classified as SOA_{nf} or SOA_{ff} by Gelencsér, May, Simpson, Puxbaum, Wagenbach, Pio, Kasper-Giebl, and Legrand may consist of high-molecular weight compounds which are still volatile at the point and temperature of emission, but which quickly condense to the particle phase. These VOC may fall outside the scope of both VOC and PM inventories, but contribute to measured TC. Robinson *et al.* [2007] have highlighted similar problems.

- Further use of tracers, such as C, levoglucosan and markers if primary biological OC (*e.g*. cellulose, sugars). Such tracers offer much greater possibilities to understand the sources of observed OC than measurements of simply the total OC or TC.

Acknowledgments

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

9. Contributions from the Participants in Group 1

Micrometeorological Measurements of Anthropogenic VOC Emissions from Urban Areas

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Emission fluxes of anthropogenic volatile organic compounds were measured above several European cities to quantify the emissions, assess the quality of emissions inventories, derive emission factors and to study the controls of the emissions.

Introduction

Emissions of anthropogenic volatile organic compounds (VOC) from area sources in the urban environment are currently highly uncertain, with most official national atmospheric emission inventories not providing a spatial breakdown of the VOCs. Even less is known about the emission of oxygenated compounds as these are difficult to measure reliably with gas chromatography. With the advent of the commercially available Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS), several groups have recently reported direct micrometeorological measurements of VOC fluxes above vegetation. However, this technique has rarely been applied above urban areas, during two studies in Mexico City [Velasco *et al.*, 2005; Tom Jobson, 2006, unpublished data].

Scientific activities

We have recently measured VOC fluxes above several European cities, including Gothenburg, Sweden (February 2005) [Nemitz, *et al.*, 2005], Edinburgh, U.K. (November 2005), Manchester, U.K. (May 2006) and London, U.K. (October 2006) and report here preliminary results of the latest measurement campaign: measurements were made from 29th September to 2nd November 2006 at a height of 200 m from the Telecom Tower in central London (51°31'17" N; 0°08'20" W). The tower has a typical diameter of 16 m. A 12 m tall lattice tower structure was erected on its flat top (Level 40), with the ultrasonic anemometer (Model R3-50, Gill Instruments, U.K.) and gas inlet mounted 3 m above the top of the lattice tower. Air for the PTR-MS analysis was sampled down a 45 m Teflon tube (3/8" OD) to the instrument on Level-35 of the building, at a flow rate of about 60 *l* pm. Simultaneous measurements included fluxes of H_2O, CO_2, CO and O_3, aerosol fluxes (total number fluxes, size-segregated fluxes and chemically resolved). The PTR-MS was set up to scan through 10 masses at 50 ms dwell time, taking just over 1 s for each scan. Each concentration measurement was paired up with the associated wind data, in a virtual disjunct eddy covariance approach [Karl *et al.*, 2002], where the time lag of approximately 5 s was obtained as the maximum in the cross correlation function. For preliminary data analysis, concentrations were calculated using reaction rate constant (k) values from Zhao and

Zhang [2004] and reaction time (t) values were calculated as $t = L/v_d$, where L is the length of the reaction chamber and v_d is the drift velocity [Lindinger, 1998].

Scientific results and highlights

This section presents some of the highlights of the preliminary data analysis. An example time-series of the concentrations and fluxes of acetone and ethylbenzene are shown in Figure 1. Fluxes show a clear diurnal pattern and are reduced at the weekend (21st and 22nd October) and largest on the Monday (23rd October). The ratio in the fluxes of these two compounds is variable.

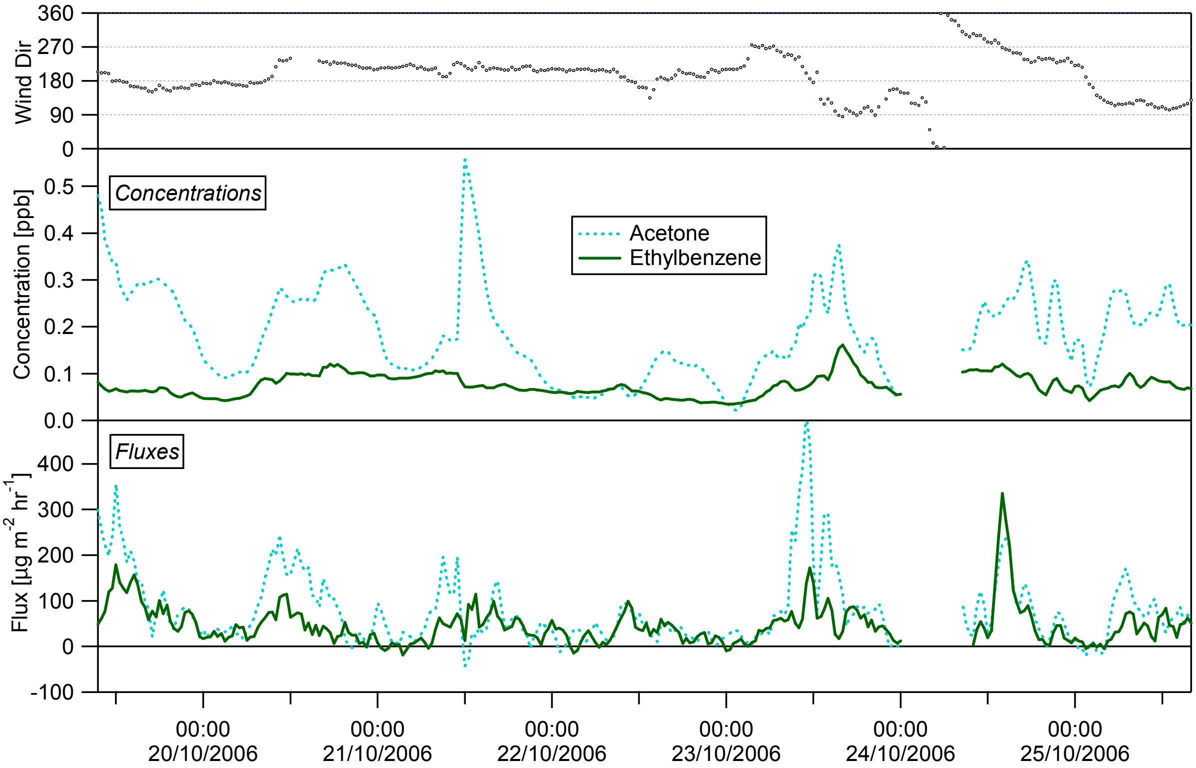

Figure 1. Example time series of acetone (derived from *m/z* 59) and ethylbenzene (derived from *m/z* 107) in relation to wind speed.

Averaged diurnal cycles for the third measurement week (19th – 26th October) are presented in Figure 2. The average diurnal patterns of the fluxes of the different compounds is roughly similar and follows the expected pattern of traffic activity in the city. The absence of a clear two-peak rush-hour pattern is consistent with earlier CO_2 flux measurements made above a city centre [Nemitz *et al.,* 2002]; rush-hour behaviour tends to be more pronounced on commuter roads. However, while traffic starts to rise around 6 am local time, as measured at the nearby Marylebone Road [AQEG, 2004], the observed emissions rise at 10 GMT (8 am local time). It is probable, that at night, due to the high measurement height, the site is de-coupled from the street-canyon activity and that fluxes are only observed as the nocturnal boundary layer breaks up in the morning.

Despite the fluxes following a similar pattern, there are also differences. For example, isoprene emissions rise later in the day, indicating that a biological control may be contributing to the emissions. Some emissions remain relatively large into the late evening hours (benzene, acetaldehyde, acetonitrile), while others decrease more rapidly (isoprene, ethylbenzene, acetone, methanol). This may be due to a change in the sources in the evening (*e.g.* larger contribution of residential heating sources, shift of the traffic composition away from HGV, larger fraction of taxi journeys) or a change in the meteorological drivers (such as surface temperature for biological and fugitive sources).

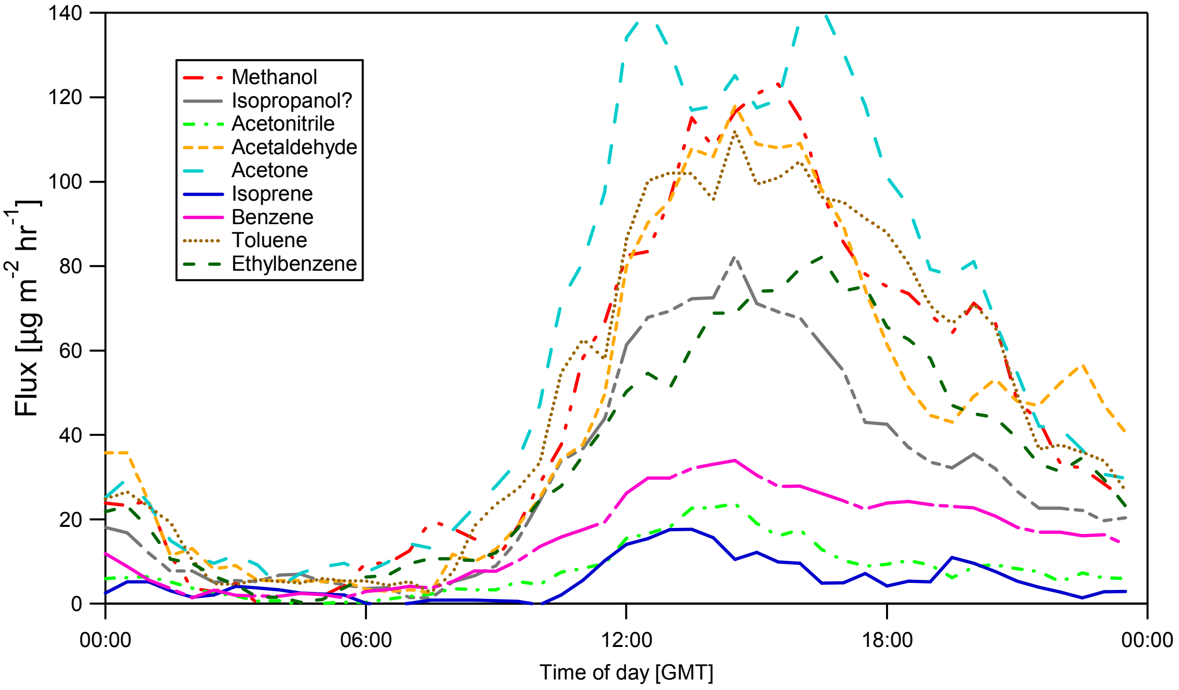

Figure 2. Averaged diurnal cycles of the flux for measurement week 19th-26th October 2006.

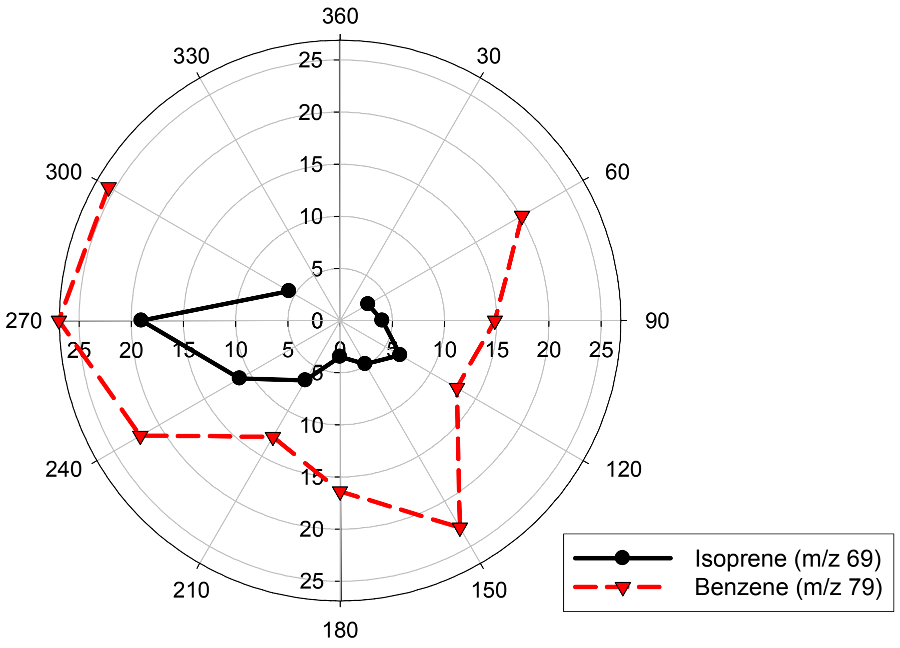

Figure 3. Wind sector dependence of the flux of isoprene and benzene (in µg m^{-2} hr^{-1}).

The different compounds also differ in their wind sector dependence. For example, isoprene shows a distinct increase under westerly conditions, possibly linked to urban park land in this direction, while many compounds, such as benzene, show a more homogeneous wind sector distribution (Figure 3). Isoprene has been reported to be emitted both from vehicle sources and from humans. However, the different behaviour of isoprene observed in this study (both in terms of temporal and spatial pattern), compared with the clearly anthropogenic gases, indicates that biogenic sources may contribute to the emission of this compound, even in autumn in a UK city.

Future outlook

The data presented here constitute only a very preliminary analysis and will need to be analysed in the context of the ancillary measurements (such as fluxes of CO_2 and CO). In addition, comparison with GC analysis of flask samples and adsorption cartridges will need to confirm the interpretation of the m/z measured with the ptr-ms. However, the data already look extremely promising and show that direct flux measurements in the urban environment by ptr-ms and eddy-covariance and possible, provide an independent assessment of emission inventories and provide information on the control of the emissions of a range of anthropogenic VOCs.

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The Direct Effects of Ozone on VOC Emission by Vegetation

Contribution to ACCENT workshop on Volatile Organic Compounds: Group 1

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Summary

Emission of methanol, acetaldehyde, acetone and isoprene from fully expanded leaves of *Populus alba x tremula* and *Fagus sylvatica* exposed at different ozone treatments was investigated under field and laboratory controlled conditions. In parallel, meteorological and plant physiological parameters were determined. The results of this study show that long-term and chronic ozone treatment had no immediate effect on isoprene emission but significantly enhanced methanol and formaldehyde emission. It was demonstrated that short-term and acute ozone exposure significantly increased isoprene, methanol and formaldehyde emission in poplar leaves. In a further set of experiments, under the site conditions of a temperate forest, the exchange of short-chained oxygenated carbonyls (aldehydes, ketones) was assessed from leaves of adult European beech trees. The crowns of the trees were either exposed to an elevated O_3 regime as released by a free-air fumigation system ($2 \times O_3$) or to the unchanged O_3 regime at the site ($1 \times O_3$, “control”). Trees exposed to $2 \times O_3$ emitted acetaldehyde and acetone at enhanced rates.

Introduction

Volatile Organic Coumpounds (VOC) play an important role in atmospheric chemistry as they strongly affect the oxidative capacity and the production of tropospheric O_3 and peroxyacylnitrates (PANs) that both perturb plant growth and human health [Kotzias *et al.*, 1997; Sakaki 1998].

The objective of this work was to study the particular influence of increased future O_3 levels on different tree species, making use of a ozone fumigation system (laboratory study) and of a free-air O_3 exposure system (field study). As a first step towards this goal, the direct effect of short-term and acute and long-term and chronic ozone exposures on isoprene emission from Grey poplar leaves (*Populus x canescens*) was characterized.

Scientific results and highlights

In laboratory under controlled conditions, leaves of Grey poplar were treated with chronic and acute ozone concentrations. The results of this experiment showed that poplar exposed to short-term and acute ozone concentration (4 h, 170 nL L^{-1}) emitted significantly higher amounts of isoprene (35 nmol m^{-2} min^{-1}) compared to controls (18 nmol m^{-2} min^{-1}), whereas the application of long-term and chronic ozone concentrations (8 h, 80 nL L^{-1}) had no effect on isoprene emission rates (Figure 1).

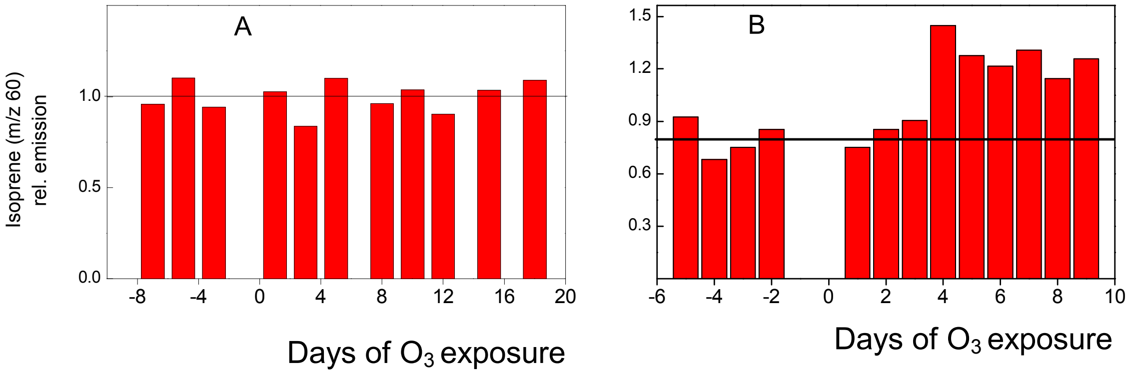

Figure 1. Effect of long-term and chronic (8 h, 80 nL L^{-1}) (**A**) and short-term and acute (4 h, 170 nL L^{-1}) (**B**) ozone fumigations on isoprene emission from single leaves of poplar (*Populus x canescens*). Each graph shows isoprene emission rates of control and ozone treated leaves (dashed area). Isoprene emission rates recorded at the same time of the day for one hour immediately after the fumigation episode are shown.

In another set of experiments, fully expanded poplar leaves exposed to chronic (80 ppb/4h) and acute (170 ppb/4h) ozone fumigation for five consecutive days showed elevated methanol and formaldehyde emission rates compared to control not fumigated leaves (Figure 2). Methanol emission increased twice in trees exposed to chronic ozone stress after five days of fumigation. Additionally, a three-fold increase in formaldehyde emission rates compared to controls was detected in chronically exposed trees (Figure 2A). Poplar trees exposed to acute ozone fumigation, a nine fold increase in methanol emission and a three-fold increase in formaldehyde emission compared to controls was observed (Figure 2B).

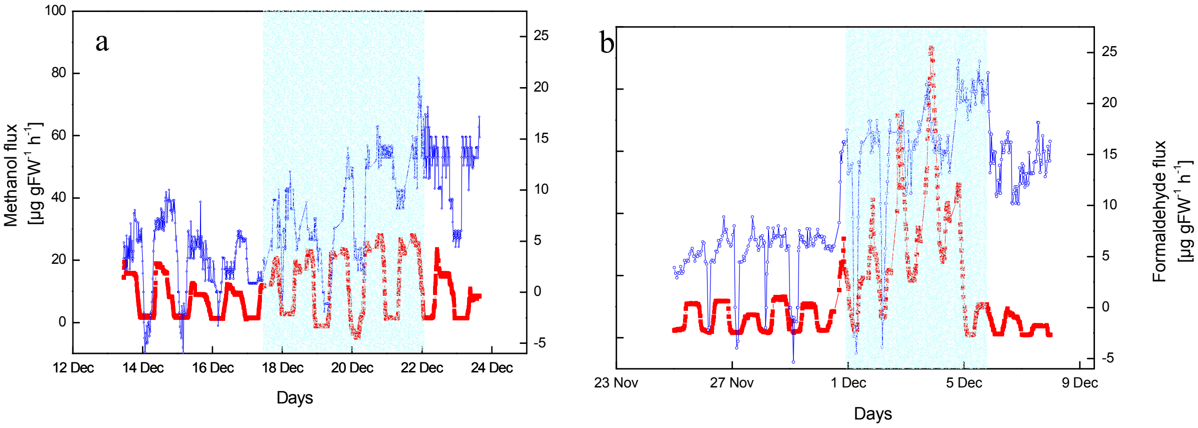

Figure 2. Effect of O_3 on methanol (red line) and formaldehyde (blue line) exchange from *Populus alba x tremula* leaves. Five months old poplar trees were subjected to chronic ozone (80 ppb/4h) (a) or acute ozone fumigation (170 ppb/4h) (b). Ozone fumigation treatment was applied for five consecutive days followed by 2-3 days recovery.

A comparison of carbonyl exchange between the trees under the 1 × O_3 and 2 × O_3 regimes revealed elevated O_3 levels to cause significantly higher rates of formaldehyde, acetaldehyde and acetone emissions (Figure 3). When viewing averages of all emission data, beech trees under 2 × O_3 emitted about 3 times more acetaldehyde (*c.* 60 nmol m^{-2} min^{-1}) than did control trees (*c.* 20 nmol m^{-2} min^{-1}; Figure 3A). The lowest acetaldehyde emission under 2 × O_3 was about 7.5 nmol m^{-2} min^{-1}, whereas maximum rates amounted to about 116 nmol m^{-2} min^{-1}. In contrast, acetaldehyde emitted by control trees (1 × O_3) ranged between 0.25 (minimum) and 46 nmol m^{-2} min^{-1}(maximum). Formaldehyde emission in trees under 2 × O_3 was with minimum rates of 4.31 nmol m^{-2} min^{-1} and maximum rates of 84 nmol m^{-2} min^{-1} almost 2.5 times higher than emissions from control trees (1 × O_3, 0.52 nmol m^{-2} min^{-1} (minimum) 56 nmol m^{-2} min^{-1} (maximum); Figure 3B). Similarly, trees under 2 × O_3 emitted approximately 4 times more acetone than did trees under 1 × O_3 (Figure 3C). Minimum acetone emission of trees under 2 × O_3 was 1.68 nmol m^{-2} min^{-1}, whereas maximum emission amounted to 99 nmol m^{-2} min^{-1} compared to 0.71 nmol m^{-2} min^{-1} (minimum) and 43 nmol m^{-2} min^{-1} of controls (1 × O_3).

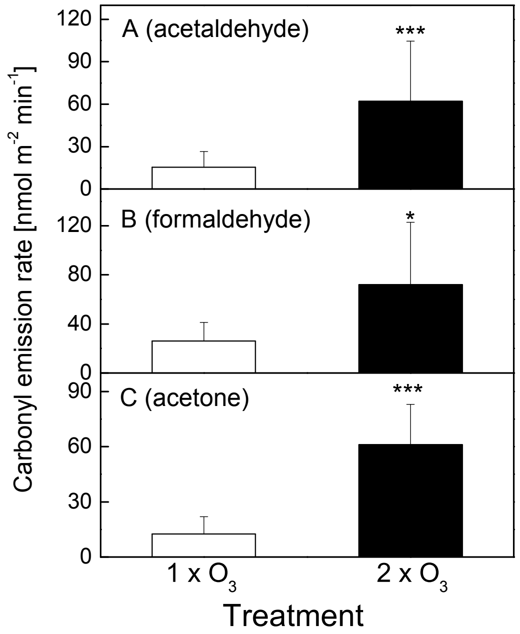

Figure 3. Effect of O_3 on acetaldehyde (A), formaldehyde (B) and acetone (C) exchange from beech leaves. Data were recorded in August 2001 and 2002 at "Kranzberger Forst". Means (± SD) of at least 15 measurements per O_3 regime with four trees each are shown. Statistically significant differences were calculated with Student's t-test for non Gaussian variables and are indicated by asterisks above bars (*, $p < 0.05$; ***, $p < 0.001$).

Future outlook

The finding that VOC emission can be enhanced by elevated ozone episodes is of particular significance for future climate change scenarios that assume increased O_3 levels. In the next year we aim to identify and quantify the physiological responses of ozone exposure in plants in which the synthesis and emission of isoprenoids has been controlled by molecular and eco-physiological tools. We will determine to what extent isoprenoid emissions have a protective effect on abiotic stresses.

The examination of the direct effects of elevated ozone on isoprenoid emissions will involve studies on membranes stability by measuring the lipid matrix (fluidity, thermostability, ionic conductance) and the generation of oxygenated stress products (hydrogen peroxide, lipid peroxidation status).

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Investigations of Primary Emissions from Vegetation of Biogenic Volatile Organic Compounds (VOC) needed to Decrease Uncertainties

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

The Biogeochemistry Department of the Max Planck Institute for Chemistry, Mainz, hosts an interdisciplinary research group focusing on the exchange of trace gases between biosphere and atmosphere. Intensive work is carried out to investigate the deposition and primary emissions on small scales with enclosures techniques. Measurements are completed by flux measurements on towers and aircrafts. Recent results lead to the conclusion that we need a much better description and understanding of primary emissions on a leaf or branch level to assess regional and global budgets as well as the effects on air chemistry and physics. For some trace gases studies are needed on a bi-directional level (deposition and uptake) to understand the net exchange.

Introduction

Plant isoprene emissions are known to be both light and temperature dependent and are modelled accordingly, but during the last decade several Mediterranean tree species were reported to emit monoterpenes triggered by light and temperature in very close relation to actual carbon fixation (BEMA, 1997). Further studies with African and European plant species as well as from first studies within the Amazonian rainforest showed that the release of isoprene and monoterpenes occurs under a very similar regulation [Kesselmeier *et al.* 1996; Loreto *et al.,* 1996; Guenther *et al.,* 1996; Kuhn *et al.,* 2002, 2004; Dindorf *et al.,* 2006]. Additionally, compounds such as monoterpenes may be stored in plant tissues with special functions which can be regarded as special cases [Kesselmeier, 2004]. Recent research delivered new insight into the biochemical pathways showing that both groups of isoprenoids are produced in chloroplasts within the same biochemical pathways [Lichtenthaler, 1999]. Hence, immediate release under regulation of light and temperature can be regarded as a common characteristic. It has been clearly demonstrated that implementing such results into modelling will significantly change budget estimates [Dindorf *et al.,* 2006; Lenz *et al.,* 2001; Moukhtar *et al.*, 2005]. Further changes might be expected taking other VOC species into account, such as methanol or sesquiterpenes, the latter being involved in plant-animal and plant-plant interactions and therefore difficult to estimate.

Scientific and technical toolbox

Despite our increased knowledge we still face significant open questions concerning the composition of VOC mixtures, quantity or seasonality which can only be answered if we go directly to the source and unravel the quality and quantity of primary emissions. Such measurements can only be performed with enclosures on a leaf or branch level (Figure 1). Within this context we investigate primary emission from European and Amazonian vegetation under natural field as well as plant chamber conditions.

Figure 1. Two enclosures (stabilised Teflon film bags), one is an empty reference, and the other one is enclosing a branch to investigate trace gas exchange between plants and the atmosphere acting like a stethoscope to listen. Emission measurements are accompanied by the determination of CO_2-exchange (photosynthetic assimilation, respiration) and water transpiration (Figure 2). Flushing air is mostly ambient but is cleaned from oxidants for the detection of reactive compound emissions.

Results, discussion and outlook

The knowledge of primary emission quality, quantity and regulation as well as the exact information on a plant species level (Figure 2) is required for any correct estimation of biogenically driven fluxes. The main open questions to be further investigated shall be addressed by a few statements.

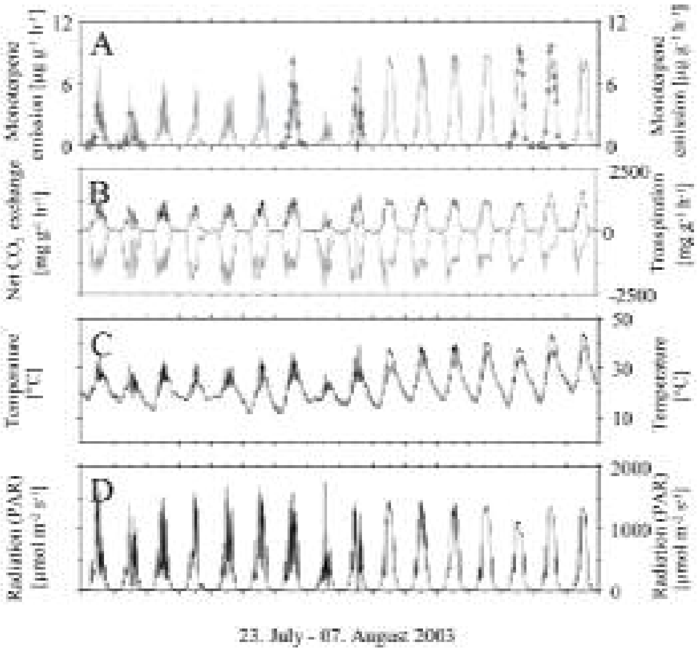

Figure 2. Diurnal course of trace gas exchange of an enclosed branch of European Beech and micrometeorological parameters measured during a field experiment in July/August 2003 (ECHO-Field Campaign, Jülich, Germany). Positive numbers indicate emission of the respective compound, while negative numbers indicate deposition. (A), Monoterpene emission is indicated by grey diamonds. Monoterpene emission calculated by application of the G97 algorithm is indicated by the grey solid line. (B), diurnal course of net CO_2 exchange (grey solid line) and transpiration (black solid line). (C), ambient temperatures (grey solid line) and leaf temperatures (black solid line). (D), photosynthetic active radiation (black solid line). For details see Dindorf *et al.,* [2006].

Primary emission quality and quantity can be easily linked to carbon exchange budgets

Enclosure measurements should always be accompanied by physiological measurements of carbon and water exchange for assessment of primary physiological processes and for stress avoidance. Relation of trace gas exchange to these primary processes will deliver information about the significance to carbon and water budgets.

Knowledge of primary emission quality and quantity is needed to discuss any flux data and chemical reactions above the canopy

Fluxes, atmospheric mixing ratios and atmospheric chemistry can only be discussed on the basis of primary emissions which have to be investigated by enclosure measurements. This way we can learn how and why the biosphere produces and emits volatile compounds. Furthermore, biological production processes should be understood as they may be of substantial importance for modelling. This way we can understand why and when volatiles are released, relating to questions concerning physiological and ecophysiological meaning such as function in plants functions, defence mechanisms, signalling and seasonality for example.

Primary emission quality and quantity is still poorly known because of compounds' chemical reactivity

We need to identify the amount and composition of the emissions. Measurements under ambient air conditions have to be compared to emissions which are not influenced by chemical reactivity. Some compounds are known to be of sufficient reactivity not to be detected under ambient air conditions. Furthermore, plants themselves may adapt to a changing oxidative environment by changing the emission pattern. Hence, emission measurements under oxidant free air must be performed in order to clarify the real release from the biosphere. Under such conditions we will have a chance to correctly measure and identify reactive and highly reactive compounds. Furthermore, we will get information about oxidation products to search for in order to clarify the influence on chemical processes in the atmosphere.

Primary emission quality and quantity is still poorly known because of missing knowledge on a plant species level

We still do not have a sufficient overview of the primary emissions from important plant species. There are numerous publications reporting about surprising emission rates and amounts from vegetation species thought to be sufficiently investigated. Existing databases contain contradicting data sets. Conflicting data may exist due to investigation under different environmental and developmental conditions. Some recent results clearly demonstrate that our knowledge might not yet be good enough to model emissions on a larger scale. We have to go back to the plant species level. European beech is one surprising example, only very recently reported as a substantial light dependent monoterpene emitter [Moukhtar *et al.*, 2005; Dindorf *et al.*, 2006], Figure 2.

Modelling and upscaling based on plant species level will significantly change our budget estimates

Knowledge on a plant species level has to be introduced into modelling, though such models will be more complex and not easy to handle. However, first demonstrations have shown that there can be significant increases expected for our model estimates. If it is too early to introduce such knowledge it will at least help to discuss the uncertainties of a model outcome in much better way. It does not help to claim that it is too complicate if we know that actual data may be highly erroneous.

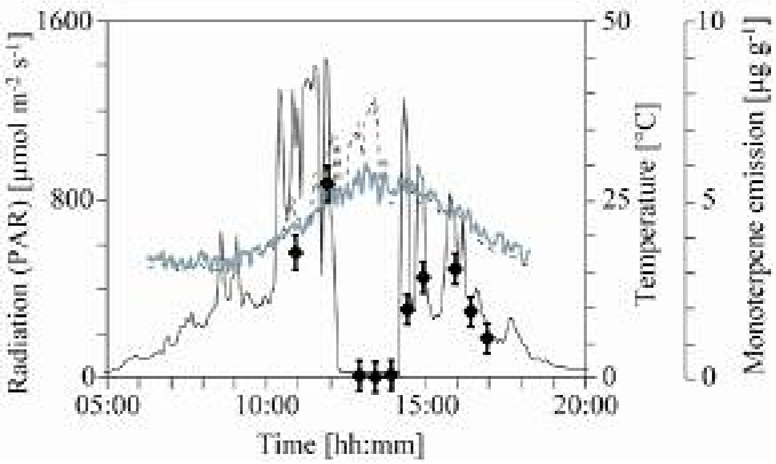

Figure 3. Monoterpene emission (grey diamonds), photosynthetic active radiation (black solid line), leaf temperature (black dashed line), and ambient temperature (grey solid line) measured prior, during and after an artificial darkening of an enclosed beech (*Fagus sylvatica*) branch under field conditions; from Dindorf *et al.* [2006].

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Methyl Bromide: Assessing the Strength of Biogenic verses Anthropogenic Emission Sources

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Introduction

Methyl bromide (MeBr) is the most abundant bromine-containing species in the free troposphere and the most important source of bromine atoms in the lower stratosphere where it can effectively carry out its ozone depleting action. MeBr, unlike other ozone-depleting gases, has significant natural and anthropogenic sources. Main natural sources include ocean, salt marshes, and wetlands meanwhile fumigation, biomass burning (since influenced by humans) and automobile emissions from burning of leaded gasoline are the main anthropogenic sources. MeBr production and consumption are regulated under the Montreal Protocol which calls for its complete phase out in 2005 in developed countries. Italy, however, asked and obtained large exemptions in critical use, i.e. cultivation of high value-added agricultural products. Smaller exemptions have been obtained by other European countries. Identification and quantification of natural sources with respect to anthropogenic ones is important because the calculated atmospheric budget of this compound is largely out of balance, with identified sinks outweighing identified sources.

Scientific activities

MeBr, along with a number of halogenated gases, is continuously measured at Mt Cimone (MtC) in the frame of the SOGE (System for Observation of Halogenated Greenhouse Gases in Europe) network. Measurements are carried out by GC-MS every three hours. Such long term measurements of MeBr in the semi-remote research station of MtC (2160 m a.s.l, northern Apennines, Italy) followed by backward trajectories (BT) analysis, can help in discriminating between natural and anthropogenic contribution, thanks to the proximity of the station to both natural (Mediterranean Sea) and anthropogenic (land based) potential source regions, and thanks to the availability of concentration data of purely anthropogenic species. However, the BT approach presents recurring problems for which possible solutions are presented.

Scientific results

In order to evaluate the capability of the BT approach to investigate potential MeBr sources, a map of potential source of a purely anthropogenic fluorinated gas such as HFC-134a is shown in Figure 1. Using a BT model, the probability of presence of a potential source is usually assigned to the whole trajectory. As a result, the Mediterranean Sea is erroneously supposed to be a potential source of HFC-134a, whereas this compound has a solely anthropogenic origin. Therefore, when sea is a real source of the compound under examination, as in the MeBr case, we have an overlapping of actual marine emission and spurious potential emission induced by the BT approach.

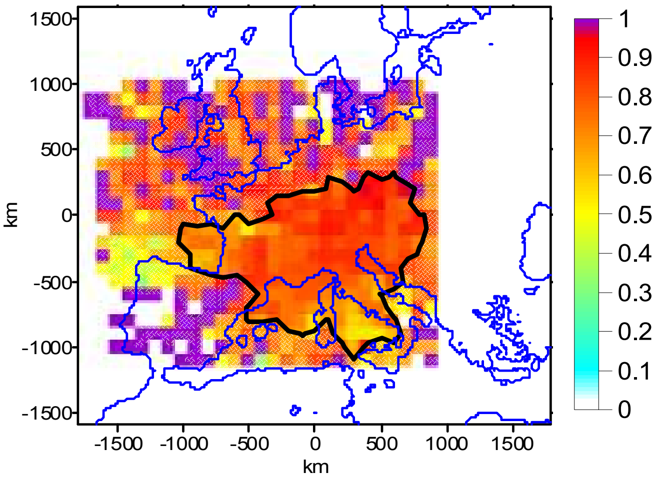

Figure 1. Potential source map for HFC-134a. Measurement unity is the fraction of marked trajectories versus all the trajectories visiting the boundary layer of a cell (100 km × 100 km). Trajectories are defined as marked if the concentration measured at the MtC station (*i.e.* the starting point of the BT) is 10 % higher than the baseline. Baseline at time t has been obtained considering the lowest concentration value in the temporal range (t ± 5 days). Continuous line contains cells which have been visited by at least 20 trajectories in a three-year period, 2003 to 2005.

The potential source map for MeBr evaluated on the base of measurements and BT approach are reported in Figures 2 which represents the ratio between MeBr marked BTs and all BTs visiting the cell boundary layer. Looking at the area inside the continuous line (*i.e.* the area where each cell has been visited by more than 20 BTs), it results a frequency greater than 40 % for the marine region. In other words, more than 4 out of 10 trajectories travelling in the marine boundary layer are characterized by high concentration values of MeBr.

Are all of them related to MeBr marine emission or some of them are MeBr continental emission travelling over the sea?

HFC measurements at MtC station highlight that HFC's sources are almost homogeneously spread in the investigated area. Therefore, in order to separate the biogenic marine emission of MeBr from the land based one, we suggest the use of high values of HFCs measured at MtC station as markers of air masses travelling over polluted continental areas.

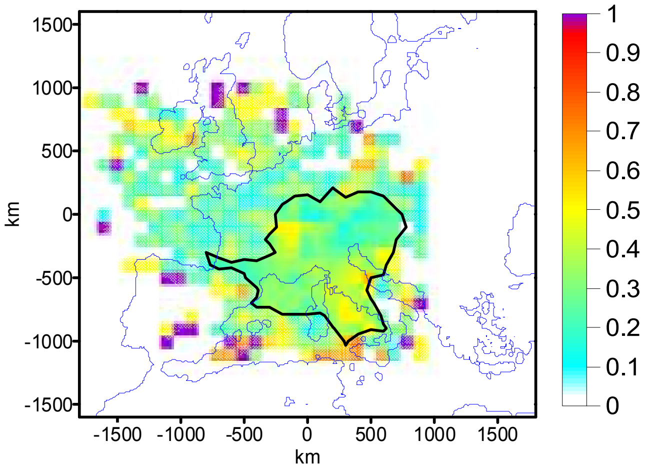

Figure 2. As in Figure 1 but for MeBr.

Figure 3 shows a map of potential marine source regions of MeBr obtained using the BTs of selected air masses characterized by concentration peaks of MeBr and by no concentration peaks of HFC-125, HFC-134a, HFC-152. Once again, we have to normalize on the total BTs for discarding effects due to climatology. When compared with Figure 2, it can be noticed how marine sources are highlighted whereas continental ones are suppressed, confirming a good efficiency of the proposed methodology. The proposed analysis suggests a minimum threshold of about 15 % for the frequency of occurrence of concentration peaks of MeBr, that is that MeBr arriving from the marine region in 15 % of cases exhibits a peak above the baseline.

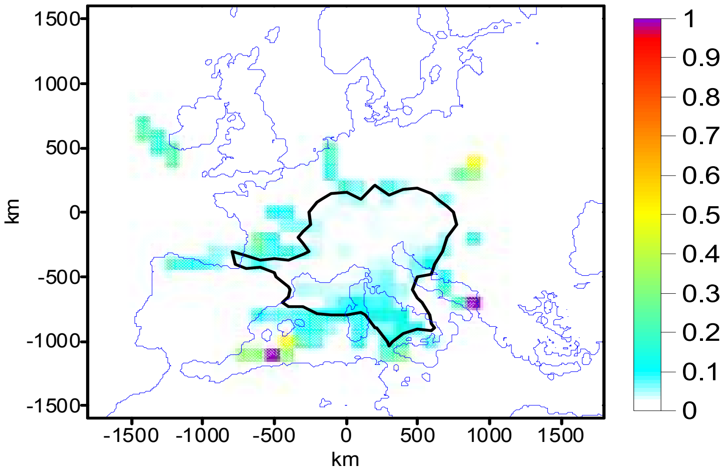

Figure 3. As in Figure 2, but for trajectories with MeBr concentration 8 % higher than baseline, and no simultaneous high concentration peaks of HFCs.

Conclusions

Potential sources of MeBr in Mediterranean area have been investigated on the base of continuously measurements carried out at MtC station and on the base of a BT approach. Atmospheric circulation induces a mixing between MeBr emitted from land based and from marine sources. In order to attempt to distinguish between these sources, a methodology using HFCs as continental air marker has been proposed. On this base, more intense continental potential MeBr sources have been localized. Moreover, the proposed approach allows us to evaluate a minimum threshold for the frequency of occurrence of high MeBr concentration events characterized by marine origin. The policy relevance of this kind of studies lies in the possibility to verify the compliance of the different countries to the international protocols aimed at regulating use and consumption of gases relevant for climate issues.

Parameterisation of Volatile Organic Compound Emissions from Plants

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

The Biosphere-Atmosphere Interactions and Atmospheric Chemistry Research group at Lancaster University has a research programme focussed upon the occurrence and behaviour of volatile organic compounds (VOC) of biogenic origin in the atmosphere. As well as isoprene (C_5H_8) and monoterpenes (C_{10}), we are interested in other hydrocarbons and oxygenated VOCs. Our work involves fieldwork, laboratory work and modelling experiments. A recent highlight of our work has been the discovery that isoprene emission from a tree (oil palm) is under robust circadian control.

Introduction

The objectives of our research are to use eco-physiological studies to investigate the role of biogenic VOCs in plant-adaptation to environmental change. From these studies we can parameterise VOC emission rates in response to abiotic and biotic stresses, or global change factors, to improve or extend currently used parameters and algorithms in emission models and inventories [Guenther *et al*. 2006]. Estimates of above canopy fluxes of VOCs are required for the assessment of past, present and future climates and quantitative Earth system studies such as carbon cycling.

Of particular interest is the flux of isoprene (2-methyl-1,3-butadiene; C_5H_8) from the biosphere because of its effect on the oxidative capacity of the atmosphere [Monson and Holland, 2001], secondary aerosol formation [Claeys *et al*., 2004] and its indirect control upon the lifetime of the greenhouse gas methane [Poisson *et al*., 2000]. Current emission models utilise a number of biological, chemical, and physical variables to estimate fluxes of isoprene but there still exists significant diurnal variations in isoprene emission that cannot be entirely explained.

Scientific activities, results and highlights

Current on-going investigations are attempting to parameterise both the biosynthesis and emission of isoprene and other VOCs when plants are subjected to biotic stress (*e.g.* herbivory) or abiotic stress (*e.g.* temperature and various forms of oxidative stress).

Studies have been undertaken investigating the effect of CO_2 growth conditions, ranging from sub-ambient mixing ratios (180 ppm; last glacial maximum) to those predicted in the future, on isoprene emissions from plants [Possell *et al*., 2005]. These studies discovered that an inverse, non-linear relationship existed between CO_2 growth conditions and isoprene emission rates generalised across different life forms (trees, grasses and herbs). When this CO_2 response curve was applied to a simple canopy emissions model, isoprene emission rates decline as CO_2 increases because the suppression of emission at higher CO_2 concentrations dominates over the change in leaf area. Furthermore, the CO_2-related suppression of isoprene emissions was seen to potentially offset the positive effects of greenhouse warming [Possell *et al.*, 2005].

Recent work with the tree species *Elaeis guineensis* (oil palm), an important crop species for the tropics, identified a novel control on isoprene emission. Experiments by Wilkinson *et al.* [2006] demonstrated strong circadian control of isoprene emission from oil palm. The diurnal cycle of isoprene emission was found to persist within constant environmental conditions with a period of approximately 24 hours and be maintained over a range of temperatures. Furthermore, molecular analysis of the biological clock showed a strong correlation with the emission of isoprene over the range of temperatures measured allowing for the possibility that this system is involved in the control of isoprene emission. The investigation by Wilkinson *et al.* [2006] also established that, in oil palm, isoprene emissions were circadian gated and were only activated at a specific phase within the 24 hour cycle. This contradicts the accepted theory that isoprene emissions are primarily light induced.

Future outlook

Continuing measurement of biogenic VOCs under different abiotic and biotic stresses, and combinations thereof, will allow us to better understand the regulations on their biosynthesis and emission and incorporate these controls into emission models. The refinement of existing parameters and algorithms or the addition of novel ones may help reduce the already substantial uncertainties that exist within current emission inventories and lead to improved predictions of air quality and climate.

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VOC and OVOC in an Urban and Background Environment

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Measurements of volatile organic compounds (VOC) in urban locations in Switzerland are used to monitor the success of measures to curb anthropogenic emissions. These long-term measurements can be used to report the effectiveness of technical measures to limit emissions as a tool for policy-makers. Measurements of oxidised volatile organic compounds (OVOC) during 4 campaigns in different seasons in Zürich were used to assess their relative importance relatively to the VOC. Actual concentrations of both groups were comparable in the urban environment. However, as OVOC only partly arise from anthropogenic sources, they are only affected by emission reductions to a limited extent. Therefore, in the future OVOC could become the dominant organic compounds in urban environments.

At the high-Alpine background site of Jungfraujoch OVOC concentrations are considerably larger than those of VOC of anthropogenic origin, such as toluene and benzene. This justifies a denser network for measurement of OVOC, ideally covered by continuous monitoring at both urban and background sites.

Introduction

VOCs have been measured in the atmosphere for about the last 50 years. First measurements have been developed together with smog periods in the 1950s in the western United States [Eggertsen and Nelsen, 1958]. In fact, these measurements were crucial for proving the contribution of the anthropogenic VOC to the ozone formation. Concentrations of the VOCs have been continuously decreased since then, due to the introduction of technical measures to curb emissions, such as the catalytic converter systems for mobile sources and the replacement of organic solvents in industrial and household applications. The decline of the concentrations has been monitored on many urban locations through the world, as VOC are relatively easy to measure by GC-FID.

On the other hand, OVOC have only lately become a point of attention. This has been enabled by further development of existing GC methods, but furthermost by new direct ionization mass spectrometers (PTR-MS).

Scientific activities

Long-term measurements of VOC in Switzerland, ranging from urban and background locations, have been used to check the effect of political measures. This was accompanied by 4 monthly seasonal campaigns in Zürich and Jungfraujoch. The influence of the OVOC on the ozone production has been found to be significant with about a third of the potential production being related to the OVOC.

Scientific results and highlights

At the suburban site of Duebendorf in the vicinity of Zürich BTX (benzene, toluene, xylenes) have been continuously measured from 1993 until present. These measurements have been performed in collaboration with the Federal Office for the Environment (FOEN). In Figure 1 yearly average concentrations are shown for the BTX in Duebendorf from 1993 until 2005. Concentrations show a common downward trend, but with an individual degree of decline for specific compounds.

In the 1990s the decline was related to the introduction of the catalytic converter systems. Whereas during this period concentrations of toluene and the xylenes have been falling at a similar rate, concentrations of benzene only have declined to a smaller amount. This can be related to the formation of benzene from toluene and the xylenes in the catalytic converter systems [Heeb *et al.*, 2002]. In the year 2000 a step change could be observed for benzene. This was related to the reduction of the benzene content in the fuel from 2 % to 1 %. The continuing decline of the concentrations after 2000 was related to the new introduction of a solvent tax in Switzerland. In general, concentrations depict the success of the applied measures for emission reductions. These results are in agreement with decreasing concentrations of anthropogenic VOCs in the industrialized parts of the world [Solomon *et al.,* 2000]. On the other hand, in the developing countries (*e.g.* in the Far East and in South America) concentrations are either growing or stable at a high level, indicating the potential for emission reductions [Reimann and Lewis, 2007].

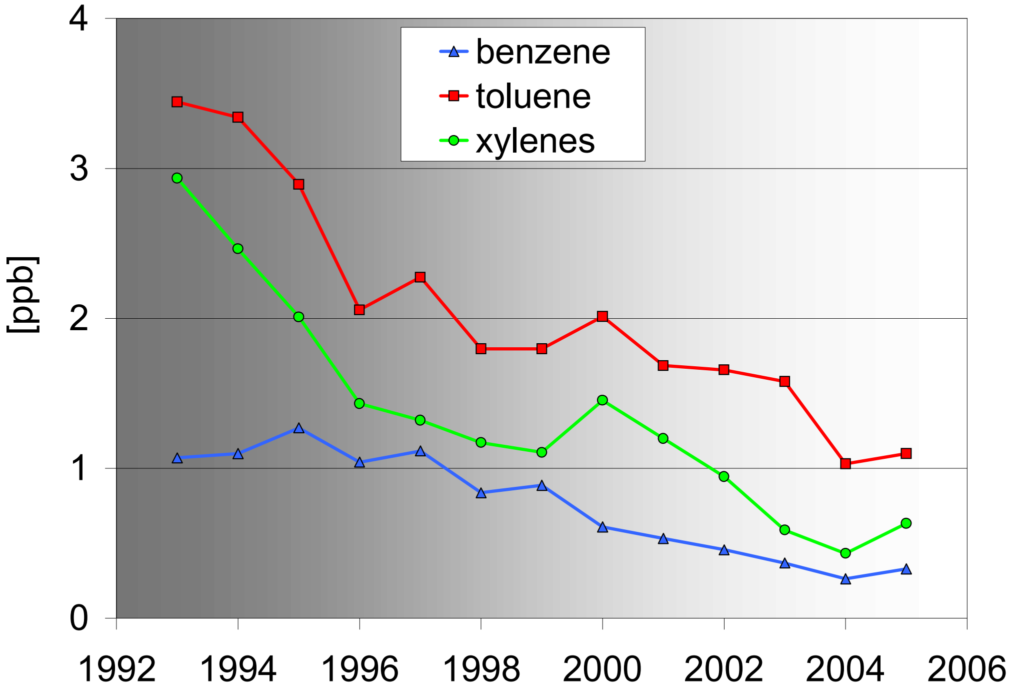

Figure 1. Annual average concentrations of BTX at a suburban site in Switzerland (Duebendorf) between 1993 and 2005. Falling concentrations document the success of introduced measures to lower emissions.

The measurement of BTX is relatively straightforward and is often promoted by environmental agencies in order to follow the success of their legislation. Therefore, continuous measurements of BTX are relatively widespread in the industrialized countries. In these countries also continuous measurements of speciated C_2-C_9 VOC are performed in order to get insight into the mechanism of photochemical ozone production.

In contrast to the VOC, no continuous measurements of OVOC do exist. This is mostly due to the more sophisticated measurement method needed. In addition, atmospheric OVOC often have a considerable fraction attributed to biogenic emissions, making them less attractive for funding bodies.

Concentrations of specific OVOC have been measured during 4 seasons, both in the city centre of Zürich and at the high-Alpine background site of Jungfraujoch. Results are shown in Figure 2. Whereas concentrations of the most abundant OVOC and VOC were comparable in Zürich, concentrations of the OVOC were considerably higher at Jungfraujoch. This is due to the more widespread biogenic sources for the OVOC coupled with a lifetime longer than transport time to the free troposphere. Concentrations of OVOC where, however, still quite high for acetone and acetaldehyde in comparison with other background measurements [Singh, 2004], which indicates the effect of the pollution events transported to the free troposphere from the European boundary layer.

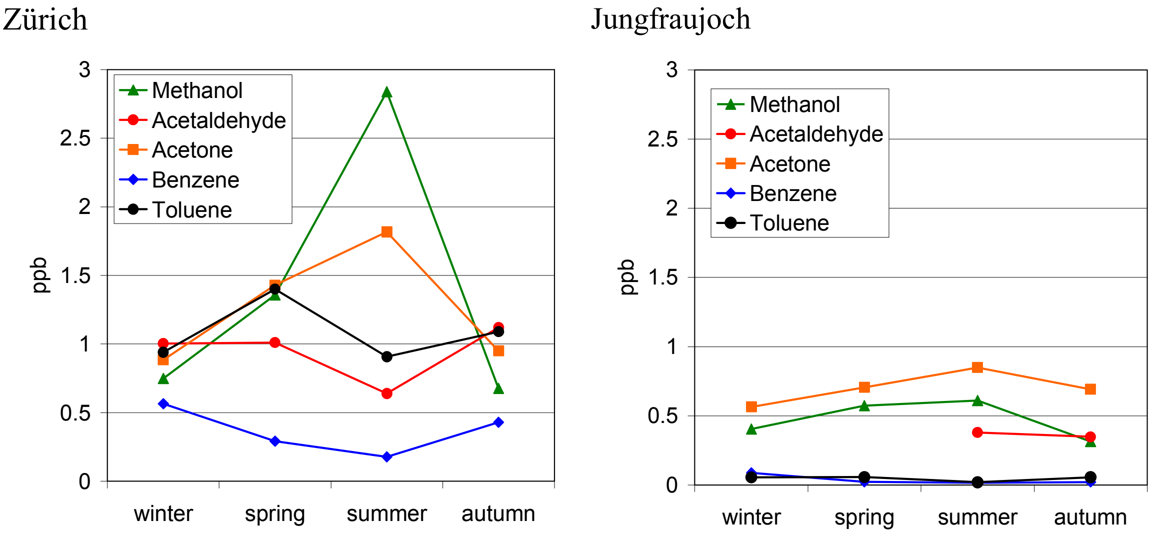

Figure 2. Concentrations of the most abundant VOCs (benzene and toluene) and OVOCs (methanol, acetone and acetaldehyde) at the urban site of Zürich and at the background site of Jungfraujoch (Switzerland).

In the polluted boundary layer the contribution of different organic compounds to the photochemical formation of ozone has been a key question of research ever since these compounds were first detected to be part of this process. In Figure 3 the contribution of different organic groups to the photochemical formation of ozone is shown for the urban station of Zürich in summer 2005. Roughly one third of the ozone formation at this location, which is representative for urban background, can be related to the OVOC.

Future outlook

The abundance of atmospheric VOCs has been studied for several decades, ranging from urban environments to the most remote places on earth. On the other hand, for the OVOC even in urban areas only data from campaigns exist and in remote areas the knowledge on the distribution of OVOC is still extremely patchy. This makes it difficult to assess their behaviour on a global scale. As anthropogenic emissions of VOC and OVOC will further decline in the future, the biogenic emissions of OVOC will get more and more important. If this goes together with a higher reactivity of the atmosphere due to large emissions, for example from eastern Asia, this could offset the efforts to lower the emissions of precursors to the photochemical ozone production.

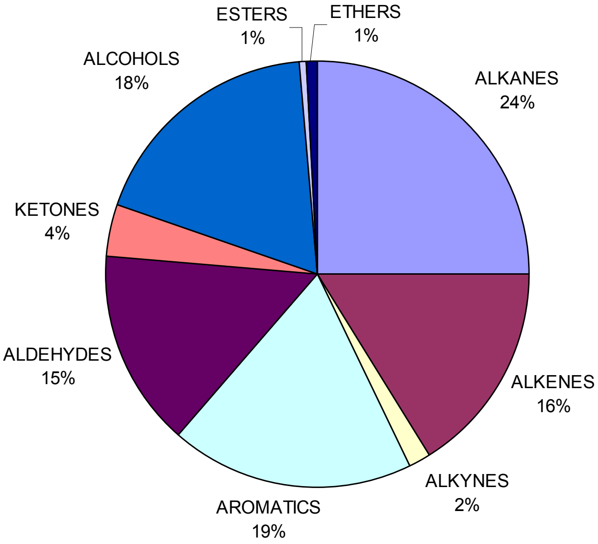

Figure 3. The contribution of different groups of organics to the photochemical ozone formation in Zürich for summer 2005.

Another group of biogenic VOC are the terpenes. They did get only limited attention in the past and have been measured only during campaigns. However, in view of the formation of secondary organic aerosols (SOA) these compounds can play a key role and have to be monitored more widely, not only during campaigns in forested areas.

Furthermore, the measurements of formaldehyde and glyoxal could play a key role in the distinction between biogenic and anthropogenic emissions on a global scale. Interestingly, these substances can also be measured by satellites [Wittrock *et al.*, 2006]. This increases their value as tracers because global coverage could be reached without having many measurements sites at different locations.

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Biogenic VOC – A Need for Deposition Estimates

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Introduction

Emissions of biogenic VOC have been studied intensively over the last two decades. Major breakthroughs in physical, physiological and biochemical descriptions of the plant production and emission process of isoprenoids have been made in the last ten years. On the other hand, significantly fewer studies have been devoted to non-isoprenoid species, particularly oxygenated VOC (OVOC), although they have been identified as significant for both atmospheric chemistry and plant biochemistry and carbon losses. Due to their properties, mostly a comparatively high water solubility and polarity, OVOC have been expected and recently also experimentally found [Karl *et al.*, 2004] to deposit back onto vegetation. However, it is currently not clear which role terrestrial deposition plays in the atmospheric budget of these species, how deposition occurs (surface adsorption versus plant uptake), and which surfaces or plant species are effective sinks for OVOC.

Activities

We have measured OVOC fluxes with PTRMS-EC and PTRMS-DEC techniques above an agricultural field in northern Germany for two years. During this time, the underlying surface was covered with bare soil, rye grass, or sugar beet. In the second year, soil OVOC exchange was followed independently with a polycarbonate chamber approximately once per week for 6 months. Enclosure measurements were carried out statically and corrected for chamber effects. The potential uptake was measured by injecting a standard containing ppm-level VOC creating an artificially high ppb-level inside the chamber.

Results

Early results showed that methanol, likely the second highest single plant emission VOC after isoprene, was the most significant component of VOC exchange over the field. Methanol's plant-atmosphere exchange has recently been studied in more detail, both in the laboratory [Hayward*, et al.*, 2004; Holzinger*, et al.*, 2000; Karl *et al.*, 2005] and in the field [Schade and Goldstein, 2001]. While we have gained an improved understanding on how methanol is linked to plant growth (pectin demethylation theory [Galbally and Kirstine, 2002]), showing higher emissions during the springtime growth phase [Karl *et al.*, 2003](Figure 1), an exponential temperature response [Schade and Goldstein, 2001], and stomatal control, we know very little about terrestrial methanol loss processes [Karl *et al.*, 2005]. Our field and laboratory studies indicate that soils can act both as methanol sources and sinks, depending on temperature and humidity. A studied agricultural soil with low carbon content emitted methanol (and acetone) when hot and dry [Schade and Custer, 2004], but acts as a sink (for both methanol and acetone) when wet, with uptake increasing with soil moisture (Figure 2). The absence of a clearly optimal uptake rate as a function of water-filled pore space as expected for a biological process might indicate that the process is a simple Henry's Law equilibrium.

Laboratory measurements on different soils containing variable amounts of moisture and carbon are still analyzed in order to elucidate the methanol soil exchange mechanism.

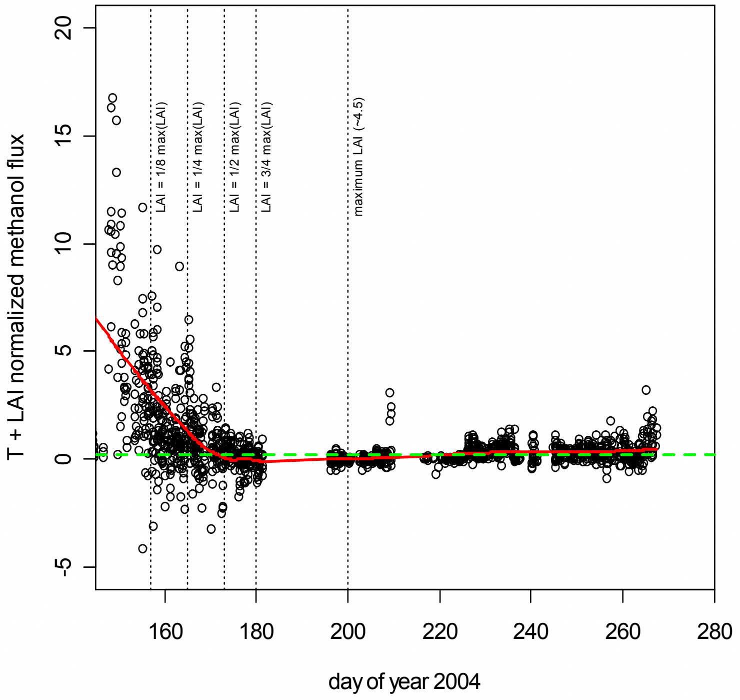

Figure 1. Temperature and LAI-normalized seasonal methanol flux from sugar beet, showing up to 5 times higher specific emissions during the early growth phase.

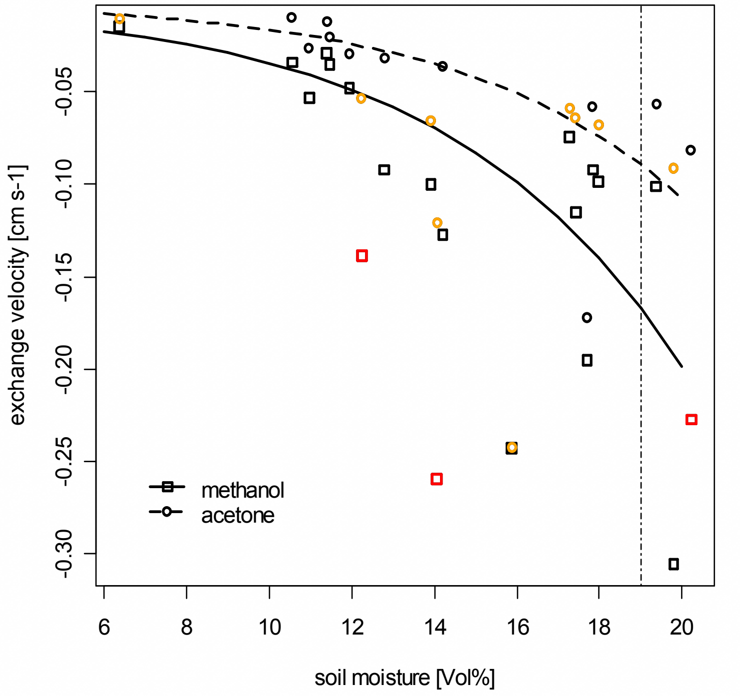

Figure 2. Temperature-normalized net exchange velocity of methanol and acetone as a function of soil moisture of an agricultural soil (vertical dashed line indicates field capacity). Potential uptake is plotted in colour.

Future outlook

To improve future VOC budgets in the atmosphere, and to elucidate total, not just CO_2-carbon fluxes between the atmosphere and terrestrial biosphere, we need to analyze VOC deposition fluxes to determine whether the deposition process is a biological uptake or a physicochemical adsorption process, which surfaces (plant versus soil) are effective in the process, and which physical or biological role these processes might have.

Our measurements show that there is a lot to learn from field data if they are carried out with sufficient duration to acquire adequate statistics, and are supplied with sufficient auxiliary data.

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BVOC Emission in the Tropics: A New Flux-tower to Assess Seasonal Variability

Contribution to the ACCENT workshop on Volatile Organic Compounds: Group 1

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Summary

Assessment of seasonal variability of BVOC emission in the tropics has been a continuous effort in the past ten years, and is still crucial in order to model the impact of these emissions at the global scale. Emissions in the tropics are known to be intense and to have a large impact at the global scale because of the deep convection occurring in these regions. Long series of isoprene and monoterpènes measurements are still lacking for most of the tropical ecosystems. We would like here to promote a recently installed flux-tower, Guyaflux, in French Guyana (South America). Two full years of energy (radiation, sensible and latent heat) as well as CO_2 fluxes are now available for that site. BVOC REA flux measurements would start at the beginning of the dry season (September 2006), and last for at least one dry and one wet season (6 months) in that configuration. Additional equipment, fast isoprene sensor and PTR-MS, might be added following this first trial period.

Rationale

Present inventories are still uncertain in assessing BVOC emissions in a large range of ecosystems, and particularly for tropical ones (primary and seasonally dry forest, woody and shrubby savannas). A large part of these uncertainties is linked to the large variability of ligneous species, and of emission factor between and among ligneous families and genus in all ecosystems, especially tropical ones. Standardizing isoprene emissions factors according to [Guenther *et al,* 1995] still result in variations covering more than two orders of magnitude ([Boissard *et al,* 2005], Figure 1).

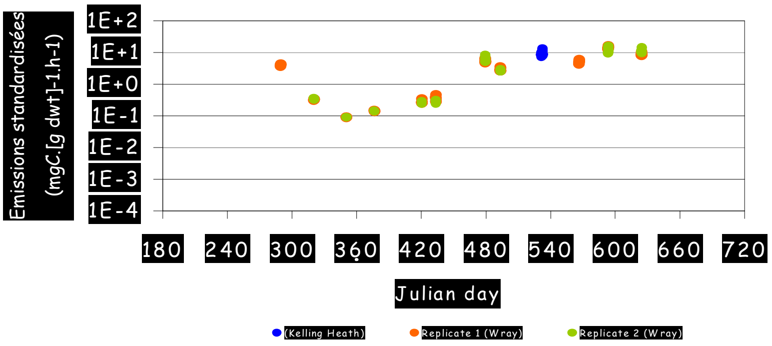

Figure 1. Seasonal variations of standardised (30 °C et 1000 mmoles.m^{-2}.s^{-1}) *Ulex europaeus* isoprene emissions measured at 2 sites in UK: Wray (two simultaneous replicates - orange and green points) and Kelling Heath (blue points).

Tropics are the place of the highest biogenic emission in relation with favourable climatic conditions (radiation and temperature), and high net primary production (resulting in high LAI and emitting biomass). However, tropical ecosystems have been under-sampled in the last twenty years. This is mainly due to difficult access, set up and maintenance of scientific experiments in those regions. Now, it should be noticed that assessing biogenic emissions in the tropics is of particular importance since they can impact large areas (up to global scale) due to deep convection (ITCZ). Modelling work [Guenther *et al*, 1999] has shown that taking into account biogenic emission would decrease OH concentration between 30 and 90 % (when HO_2 and H_2O_2 concentrations would increase in the same time). In the same time, isoprene and any other pre-existing compound in the boundary layer reacting with OH see their lifetime multiplied by a factor of five. Reducing emission of a factor two reduces isoprene lifetime of a factor 1.6.

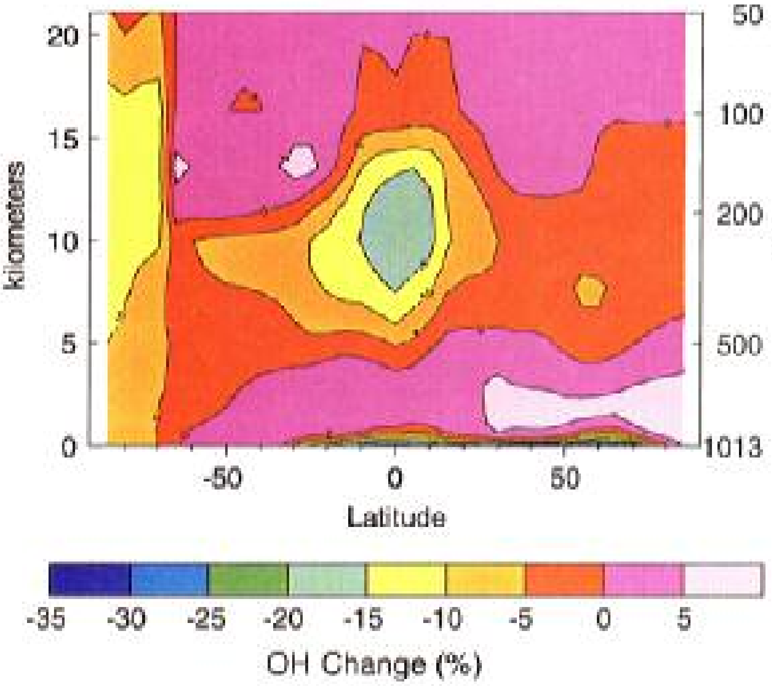

Figure 2. Percent difference in the July zonal average vertical distribution of OH predicted by IMAGES for scenarios with isoprene and without isoprene

OH concentration decreases between 10 and 20 % in the equatorial region for altitudes between 7 and 12 km (Figure 2). This has strong implications since any change (or uncertainties) in the biogenic emissions in the tropics could change the lifetime of long-lived and long-distances transported compounds such as methane. Decrease of OH concentration lead to an increase on ozone concentration of about 10 % in the atmosphere just above the source, and between 25 and 50 % further.

Parameterizing BVOC emissions at the canopy scale, the scale of fluxes used as inputs in chemistry-transport model at regional or global scale, is a difficult task due to the large 1- variability of emission factor (as mentioned above) 2- number of influential parameters. Both can impact the biogenic emissions at different time scale, from hours to weeks. Variability of climatic conditions are well-marked in the temperate regions, and usually have a clear influence on the biogenic emissions, though low frequency variation have not been incorporated in most of the studies of emission impacts on atmospheric chemistry. Parameterizing BVOC emissions in the tropics can be more difficult, but very few studies have focused on that objective. Climatic conditions (daily mean temperature and PAR) in the tropics show little variation along the year. Measurements of isoprene emission made in central Africa (Congo, [Serça *et al*, 2001]) showed that emissions could vary of a factor three (Figure 3) for two different periods of the year (March, end of dry season, and December, end of wet season).

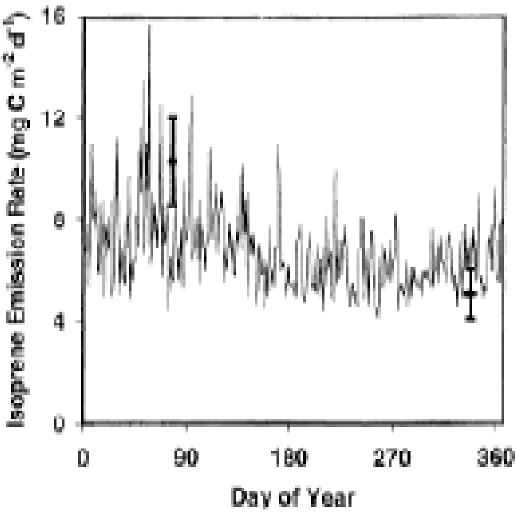

Figure 3. Daily total isoprene emission simulated and measured (with standard deviation) for the two field campaigns (March, end of dry season, and December, end of wet season).

Figure 3 shows the change in daily total isoprene emission linked to the evolution of temperature and PAR. These emissions can also vary of a factor two from one week to the other. Note that temperature and PAR were similar for the March and December experiments. This means that the observed difference is not linked to the change in these parameters. A possible explanation would rely on a lower stomatal conductance in March, leading to a higher leaf temperature and isoprene emission. Evaporation was indeed lower in March than in November, indicating a lower stomatal conductance in the first case, coupled with lower plant water potential (not measured). CO_2 fluxes were also lower in March, this being consistent with a lower stomatal conductance and a higher leaf temperature. In tropical conditions, increase in leaf temperature is effectively followed by an increase in isoprene emission, and conversely, by a decrease in photosynthesis.

Guyaflux flux-tower

A flux tower site (Guyaflux, see Figure 4) has then been set up in 2003 in an undisturbed tropical rainforest in French Guiana (5° 16' 54" N; 52° 54' 44" W), where mean annual rainfall is high (3000 mm on average) and severe seasonal dry seasons (at least three consecutives months with less than 50 mm rainfall), not necessary associated with ENSO events, are frequent. Two full years (2004 and 2005), contrasting in terms of dry season length and intensity, have been sampled so far. The tower equipment includes a complete automatic weather station, Licor 7500 + Licor 7000 + Sonic Anemometer Gill R3-50 providing energy balance (sensible and latent heat) as well as CO_2 fluxes. Additional ground measurements include: 10 stands (0.49 ha) located in the footprint of the flux tower (about 50-100 ha) with all trees with dbh > 10 cm identified, labelled and mapped (3000 trees), 4 litter traps per stand, 8 automatic soil respiration chambers, and soil water content at the footprint level.

Analysis of this whole set of measurements suggests that the ecosystem is acting as a net carbon stock for the atmosphere, at a rate of about 1.5 tC ha^{-1} an^{-1}. Strong seasonal variations in NEE are observed with environmental conditions during the dry periods and ecosystem respiration being the main determinants of the annual net carbon balance.

Carbon storage is more important 1) when daily total PAR is maximum, as during a severe dry season where cloudiness is low, and 2) when ecosystem respiration, particularly soil respiration, decreases following soil water content decrease.

Figure 4. The Guyaflux flux-tower

We would like to install a REA (Relaxed Eddy Accumulation) prototype for the measurements of BVOC fluxes. These measurements could start at the beginning of the next dry season (September 2006), and last at least one dry and one wet season (6 months) in that configuration. More equipment, fast isoprene sensor and PTR-MS might be added following this first trial period. With the existing set of measurements, we will look for correlations between carbon storage, plant water potential and BCOV emission at the daily as well as seasonal scales.

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Biogenic (O)VOC – Global Climate Change Effects

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Introduction

Although a large body of literature has accumulated on biogenic isoprenoid and other VOC emissions in the last decade, leading to a significantly improved understanding of biochemistry and physiology of emissions, only few studies have addressed future changes. Due to global climate change, biogenic VOC emissions are expected to change in response to increases in ambient [CO_2], and likely also [O_3] increases in ambient temperatures changes in plant hydrological environment (more droughts and floods)

Only isoprenoid emissions have been studied under some of the expected scenarios, such as increased ambient temperatures and [CO_2] [Pegoraro *et al.*, 2005], and large uncertainties exist as to the net response on VOC emissions. A few studies are underway that investigate the response of non-isoprenoid VOC to global change parameters [Beauchamp *et al.*, 2005; [Kreuzwieser *et al.*, 2006], but there is no large-scale effort yet. Because biogenic VOC emissions exert a very significant influence on atmospheric chemistry, it is crucial to identify the responses and feedbacks of the terrestrial vegetation to anthropogenically induced climate change. If VOC emissions dropped as a result of increasing [CO_2], a negative feedback may alleviate chemical changes, if emissions increased as a result of warming and increased LAI, a positive feedback could lead to more drastic changes in atmospheric chemistry.

Activities

The first author was sponsored by ACCENT to carry out selected enclosure studies of green leaf VOC emissions under different fumigation scenarios at the University of Lancaster, UK, Department of Environmental Science, under the auspices of Professor Nicolas Hewitt. A new methanol/formaldehyde instrument developed in Bremen [Solomon *et al.*, 2005] was used to follow the exchange of these trace species when exposing plants to different ambient ozone mixing ratios in dynamically operated glass chambers.

Results

Methanol and formaldehyde fluxes were controlled by stomatal opening as indicated by strong correlations with stomatal conductance. Methanol flux also increased near-exponentially with leaf temperature similarly as shown in previous studies [Hayward *et al.*, 2004; Holzinger *et al.*, 2000; Schade and Goldstein, 2001]. The example below (Figure 1) shows the response of poplar leaves (*Populus alba x tremula*) to a chronic ambient ozone exposure (80 ppb for 4 h per day). After fumigation started on 17th December, the leaves started to emit more methanol and, with a delay, also more formaldehyde. Acute exposure to 170 ppb ozone for the same time duration per day lead to even more drastic increases in methanol emissions, possibly as a result of an internal "repair" mechanism. Assuming that ozone confers damage to cell walls, both cell degradation and new cell growth may explain the observed methanol flux increase

[Kreuzwieser *et al.*, 1999], a process that subsides again when the cause of damage (ozone) is removed.

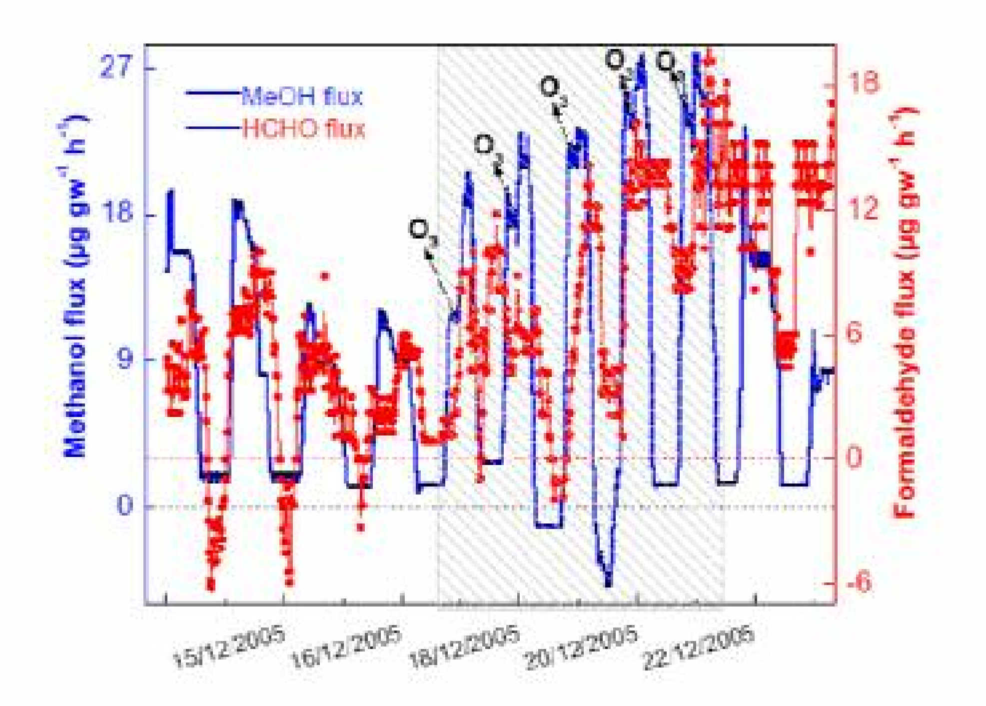

Figure 1. CH_3OH and HCHO exchange of poplar leaves before and after chronic ozone fumigation (80 ppb for 4 h per day).

Future outlook

In a climate change scenario with increased boundary layer ozone abundance, higher formaldehyde emissions could further enhance ozone formation, while higher methanol emissions can lead to higher upper tropospheric ozone formation, creating a teleconnection between the boundary layer and the upper troposphere. More work is needed to establish connections and feedbacks such as this one in order to avoid further unpleasant "surprises" that anthropogenic climate change may bring on.

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Biogenic VOC Emissions in Europe: Latest Achievements and Future Research

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Biogenic Volatile organic compounds (BVOC) play a key role in atmospheric chemistry and thus in air quality. In recent years national and international integrated research efforts significantly improved knowledge about biochemical synthesis of BVOC, genetic and environmental control mechanisms, the chemical compound pattern emitted, the oxidation pathway in the atmosphere as well as the spatial distribution of emission sources in landscapes and their hourly, daily, seasonal and yearly variation. This includes the development and continuous update of instrumental tools, analytical methods as well as modelling approaches [Steinbrecher, 2006]. In the BEWA2000 project selected BVOC emission sources, the fate in the forest atmosphere of compounds emitted, the transport of primary and secondary substances including particles, and the consequences for modelling regional BVOC emission have been investigated. It is highlighted that for air chemistry in Germany biogenic monoterpenes are much more important than thought before with feedbacks to ozone production as well as secondary particle formation and particle physicochemical properties in the lower atmosphere. But despite the great progress made in the past years still major gaps exist in particular on the emission of sesquiterpenes and other VOC than isoprenoids from vegetation. In consequence, the current view of BVOC in reactive carbon-turnover in the earth system may be different in future.

Introduction

The major emission sources of biogenic VOC are forests. Together with anthropogenic NO_x and VOC emissions, BVOC contribute to regional and global changes in the HO-radical budget, ozone as well as particle distributions with consequences on the solar radiation budget on the earth surface and in the atmosphere [Hoffmann *et al.*, 1997]. Thus it is of paramount importance to quantify biogenic sources of VOC in the most accurate way having in mind that more than 1 Gt carbon per year is involved – approximately 90 % of the total VOC load to the global atmosphere - or in other words about 1 to 2 % of the carbon annually taken up by terrestrial vegetation [Steinbrecher and Smiatek, 2004]. Despite of the great progress achieved in the past 10 years on quantifying the VOC emission by investigating the VOC compound pattern emitted by plants, studying the pathway of synthesis and genetic, physiological and environmental factors of emission control, as well as the fate and effects of BVOC and secondary products in the atmosphere, still large uncertainties exists in particular in quantifying the emission of important particle precursors such a sesquiterpenes and other VOC than isoprenoids. Thus, the understanding of BVOC induced effects in the atmosphere remains rather vague, in particular on the OH-radical budget, the ozone/particle production, particles physicochemical properties and solar radiation transfer processes to the earth surface.

Scientific Activities

The overall goal in biogenic VOC research in the last years focuses on reducing uncertainties in quantifying isoprene and monoterpene emissions from vegetation. This included studies on biochemical synthesis pathways starting at gene level from activation, transcription control for enzyme production and activity, environmental control of isoprenoid emission, transport in complex forest canopies including oxidation process in the atmosphere leading to secondary products. Two large integrated projects ECHO (http://www.fz-juelich.de/icg/icg-II/echo/) and BEWA2000 (http://imk-ifu.fzk.de/bewa2000/) took up the challenge to elucidate the complex network of different processes of BVOC exchange between forests and the atmosphere. Other projects and networks such as ISONET (http://imk-ifu.fzk.de/isonet/) and VOCBAS (http://www.esf.org; search for vocbas) further contributed to deepen our understanding of biogenic VOC production and emission. Altogether these activities beside others lead to more than 30 scientific papers - visit corresponding web-sites for accessing article titles - published in reviewed journals in recent years. In the following some highlights from the BEWA2000 projects will be presented. For detailed information it is referred to a Special Issue of Atmospheric Environment [Steinbrecher, 2006].

Scientific results

Biological processes related to VOC production in plants

In situ photosynthesis is one major carbon source for isoprenoid synthesis in plants. It was demonstrated that the flux of photosynthetic intermediates through the plastidic isoprenoid pathway is controlling short-term variability of the isoprene emission. Under CO_2 limiting conditions isoprenoid biosynthesis may serve as an alternative sink for primary products of net-photosynthesis [Magel *et al.*, 2006]. But also carbon (C) from carbohydrates transported in the xylem and starch may act as C sources under certain physiological conditions for isoprene synthesis - predominantly when net CO_2 assimilation is reduced resulting from stomata closure limiting CO_2 uptake - as shown by feeding poplar and oak leaves with [^{13}C]glucose [Kreuzwieser *et al.*, 2002]. Also plants under stress, wounding, draught, high temperature and light impact the VOC compound emission pattern from plants to a large extend resulting in increased emissions of mainly oxygen containing compounds [Loreto *et al.,* 2006].

Oxidation of monoterpens in the atmosphere

The oxidation mechanisms and aerosol forming potential of α-pinene and limonene reacting with NO_3 radicals under conditions close to atmospheric conditions were investigated in the European photo-reactor EUPHORE. Additional experiments were performed in small-scale photo-reactors [Barnes *et al.*, 2006]. Experiments were conducted in the absence and presence of both inorganic and organic seed aerosols. Pinonaldehyde and endolim were identified as the major reaction products of NO_3 + α-pinene and limonene oxidation, together with large amounts of yet unidentified organic nitrates. But the reported compound α-pinene oxide could not be identified. Reaction mechanisms for NO_3 + limonene and α-pinene have been proposed. The work suggests that the total SOA mass observed from NO_3 + limonene originates mainly through the secondary chemistry of endolim, whereas for the NO_3 + α-pinene reaction pinonaldehyde has a small SOA mass yield, and so other compounds will have more impact on the total particle mass in α-pinene experiments. An effect of aerosol acidity on SOA formation in the reaction cascade α-pinene/ozone/seed-aerosol is clearly observable resulting in higher SOA yields at lower pH values [Iinuma *et al.*, 2003].

Field experiment Norway spruce forest

At the Norway spruce field-site Waldstein, Fichtelgebirge (50°08'32" N, 11°52'04" E, 775 m a.s.l.), soil and leaf primary emission as well as canopy exchange (net emission and net deposition) of gases (isoprenoids, carbonyls, peroxides, ozone) and particles were quantified using latest eddy covariance and analytical techniques [Steinbrecher *et al.*, 2004; Klemm *et al.*, 2006]. Local and regional effects on atmospheric trace gas compositions were studied. The Waldstein data were used to validate and improve models on gas and particle exchange between the vegetation and the planetary boundary layer. A rigorous quality assurance/quality control plan was implemented for making data of different groups comparable. For joint data analysis typical summertime conditions with various wind directions, NO_x mixing ratios between 2 and 10 ppb, and O_3 mixing ratios ranging between 13 and 98 ppb were selected. Diurnal dynamics of the boundary layer governed trace gas levels in the atmosphere in addition to chemical processes such as O_3 production, and deposition. Daily cycles of atmospheric turbulence were explained by thermal production during daytime and calm conditions during night-time excluding windy conditions leading to horizontal advection of air masses intruding to the trunk space resulting from the patchiness of the forest. But most conditions could be described by a one-dimensional model for the vertical exchange processes.

Isoprenoid leaf level fluxes and ecosystem level fluxes agreed well with maximum emissions during daytime [Grabmer *et al.*, 2006; Graus *et al.*, 2006]. Particle exchange between the forest and the atmosphere was strongest during daytime dominated by particle deposition as indicated by *in-situ* flux measurements (Figure 1) [Held and Klemm, 2006]. During particle formation events starting in the morning a typical banana like growth-form of particles was observed. Theoretical considerations indicate a considerable contribution of BVOC oxidation products to the observed condensational growth. Detailed analytical studies on the chemical composition of different size classes of particles present in the forest atmosphere reveal many oxidation products of monterpenes supporting the theory [Plewka *et al.*, 2006]. The isoprene oxidation products 2-methylthreitol and 2-methylerythritol in the particles highlight the contribution of isoprene oxidation products to particle growth in the atmosphere. Pinic acid concentrations were higher in particles from above the forest canopy likely resulting from *in situ* oxidation of α-pinene with ozone.

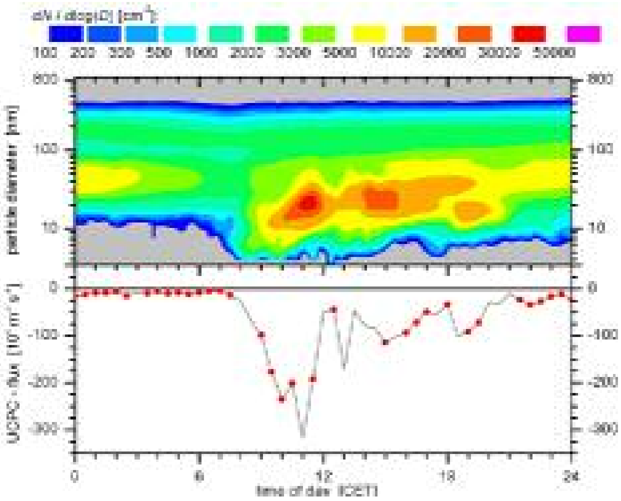

Figure 1. Particle size distribution (upper panel) and particle flux (lower panel) for a Norway spruce forest (Waldstein, NE-Bavaria, Germany) on August 2nd, 2001 using a twin CPC eddy covariance system [Held and Klemm, 2006].

Model development

An integrated semi-empirical model system for setting up BVOC emission inventories (seBVOC) has been developed operating flexible on different spatial scales, addressing hour to hour, day to day and year to year variability [Smiatek and Steinbrecher, 2006]. The model platform is integrated in a geographical information system (GIS) and a relational data base management (RDBMS) environment of input data processing, model running, and visualization. Databases compiled contain land cover and forest distribution, foliar biomass density and leaf area index (LAI) values including chemical compound and new plant specific emission factors in particular for beech [Moukhtar *et al.*, 2005; Dindorf *et al.*, 2006; Holzke *et al.*, 2006]. Meteorological input parameters were obtained using the non-hydrostatic meteorological mesoscale model MM5. The semi-empirical BVOC model (seBVOC) uses these parameters as input. Further, seBVOC considers seasonality of the emission factors, light extinction within the canopy as well as leaf temperature, air humidity, wind speed, and solar angle.

A new 1D-canopy-chemistry-emission model (CACHE) considers updated emission factors for isoprenoids and carbonyls from latest plant enclosure studies as well as complex degradation pathways with updated oxidation mechanisms for isoprene and monoterpenes [Forkel *et al.*, 2006]. Integrated layered modelling of source strength chemical oxidation and transport in canopy showed that BVOC fluxes into the atmosphere are 10–15 % lower than the emission fluxes calculated on a branch basis due to chemical BVOC oxidation within the canopy. In the lower part of the canopy, NO_3 radical chemistry astonishingly makes up a significant part of the oxidation power in the forest atmosphere even during daytime. But simulations also demonstrate that current understandings of emission, transformation, production and deposition processes of aldehydes and ketones are very limited.

A process-based model of VOC emission from plants considering substrate availability and enzyme activity has been improved and extended to capture not only isoprene but also monoterpene emission from plants without any considerably storage tissue [Grote *et al.*, 2006]. Such a model has a great potential in particular in accounting for plant stresses such as drought impacting BVOC emission potential which otherwise would require a laborious re-parameterisation of current semi-empirical models.

Regional biogenic VOC emission estimates

A chemical compound specific BVOC emission inventory of Germany based upon tree species distributions showed an average BVOC emission of 366 Gg, with 40 Gg isoprene, 188 Gg monoterpenes, and 138 Gg other VOC (OVOC) for the period 1994 to 2003 [Smiatek and Steinbrecher, 2006]. The dominating emitter types are Norway spruce (*Picea abies* L. [Karst]) forests contributing approximately 40 % to the total BVOC load in Germany. In the decade investigated, annual BVOC emissions varied in the range of ± 20 % (Figure 2). However, during specific episodes and smaller scales (Bavaria < pine/oak forest in central Germany) BVOC emissions may exceed the 10years average by 150 % as demonstrated for the hot summer in 2003. Modelled emission rates for a Norway spruce forested area compare well with measured BVOC fluxes within the uncertainty range of model and measurements (± 50 %). The new BVOC emission inventory for Germany questioned previous ones [Simpson *et al.*, 1999] as there annual isoprene emissions are overestimated by 66 %. In consequence, German forests may contribute less to ozone production resulting from isoprene oxidation in the atmosphere as previously thought.

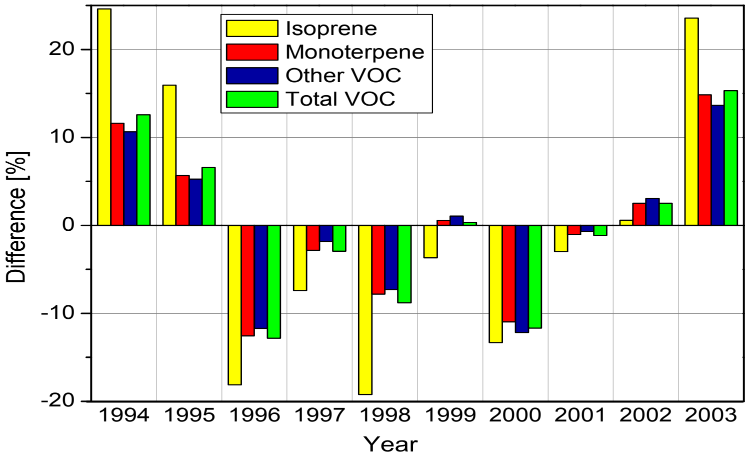

Figure 2. Annual variability of isoprene, monoterpene, other BVOC and total BVOC emissions in Germany in the decade from 1994 to 2003. Shown is the deviation from the 10years average [adopted from Smiatek and Steinbrecher, 2006].

Future outlook

Despite of the great progress made in understanding BVOC emission from vegetation in the last years uncertainties in BVOC emission inventories are still greater as factor of two demonstrated by sensitivity studies as well as validation experiments [Smiatek and Steinbrecher, 2006]. Uncertainties are especially high for emission estimates of oxygen containing compounds and sesquiterpenes being beside others potential players in atmospheric particle processes. It cannot be ruled out, that particles with a biological background exhibit different physicochemical properties impacting on, for example, radiation transfer, and cloud forming processes including feedback loops in the atmosphere in a yet unknown way. In the following years anthropogenic VOC emissions are going to be reduced further and thus biogenic VOC emissions will gain increasing importance in triggering the radical turnover in the lower troposphere in particular having in mind changed land use resulting from reforestation programs using high VOC emitting tree species (*e.g.* Eucalyptus or Popular) or turning grassland into bio-fuel cropland.

In other words, major efforts have to be put on research focusing on (1) biochemical synthesis, genetic and environmental emission control including stress effects, (2) flux studies on different spatial and temporal scales preferably long-term observations at existing sites of the global flux network, supported by (3) investigations of the BVOC oxidation in the atmosphere for elucidating short-term and long-term effects on air quality (*e.g.* contribution to ozone background levels) and climate including investigations on (4) feedback processes between the different compartments of the earth system impacting BVOC emission in the biosphere.

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NMVOC Emissions from Anthropogenic Sources in Germany

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Introduction

Emissions of non-methane volatile organic compounds (NMVOC) still contribute significantly to current air pollution problems. They are responsible for the formation of photo-oxidants such as groundlevel ozone – in connection with nitrogen oxides (NO_x) in the presence of sunlight – and individual NMVOC (*e.g.* benzene) do have adverse health effects on their own account. NMVOC are partly responsible for the depletion of stratospheric ozone as well as for the reinforcement of the greenhouse effect as precursors of ozone, which is a greenhouse gas as well. The major anthropogenic NMVOC sources are road transport and solvent use. Among these, solvent use emissions currently account for about 50 % of all anthropogenic NMVOC emissions in Germany. Figure 1 displays the distribution of NMVOC source groups in Germany.

In 1998, biogenic sources emitted approximately the same amount of NMVOC as road transport. Other NMVOC emissions mainly originate from production processes, combustion in industry and public power plants and from small combustion in households and commercial buildings.

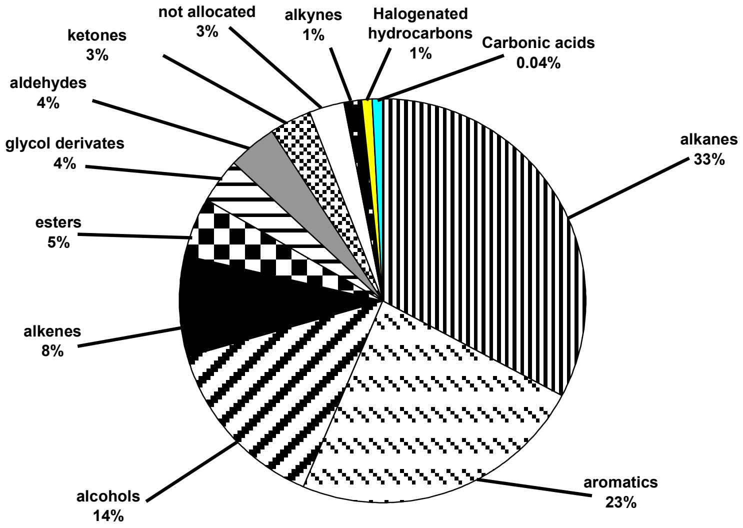

Figure 1. Disaggregation of the anthropogenic NMVOC emissions from all sectors into substance classes in Germany [Theloke and Friedrich, 2006].

Scientific activities

The overall issues in anthropogenic NMVOC emissions in the last years focused on reducing uncertainties, validation experiments and sensitivity studies. Another focus was on the improvement of spatial, temporal and species resolution of NMVOC emissions.

Results and highlights

About half of the VOC emissions in Germany 2000 were aliphatic and aromatic hydrocarbons. Oxygen-containing VOC alcohols, especially isopropanol, are the main fraction, the rest consists of alkenes, esters, glycol derivates, aldehydes and ketones, to a smaller part also alkynes and halogenic hydrocarbons. About 3 % of the emissions could not be allocated. [Theloke, 2005].

Obviously, the different source groups possess quite different split vectors or 'finger prints'. Combustion processes typically emit pure hydrocarbons and in addition – as oxygen containing compounds - aldehydes. Solvents consist of other oxygen containing VOC groups like alcohols, esters, glycol derivates and ketones. In addition the pure hydrocarbons in solvents are different from those in exhaust or flue gases, as they on the average usually possess more carbon atoms. Production processes are a very inhomogeneous group of processes with many different VOC splits.

What can be done in addition is to compare generated emission data with measured ambient concentrations. However such results would contain several reasons for uncertainties apart from those of the VOC split:

* uncertainty of the emission estimate for total NMVOC;

* uncertainties of the modelling of transport and chemical transformation from emission to measurement site;

* measurement uncertainties; and

* uncertainty for a split into single species and not species classes as selected single species are measured.

Nevertheless in the following we show results of such comparisons, as these give a feeling for the overall uncertainty for modelling VOC species concentrations and thus a sort of upper limit for the uncertainties of the VOC split vectors. Results from two evaluation experiments in Augsburg (EVA: Evaluierungsexperiment Augsburg) [Kühlwein *et al.,* 2002; Mannschreck, 2000; Friedrich and Reis, 2004] and Paris (ESQUIF: Etude et Simulation de la QUalitÈ de l'air en Ile de France) [Vautard *et al.*, 2003] are shown. The EVA experiment was carried out in March und October 1998, ESQUIF in summer 1999. An example of the results of these evaluation experiments are shown in Figure 2. The ratio of modelled to measured ambient air concentrations is shown, each as ratio to the modelled respectively measured ambient air concentrations of CO for different important species.

Figure 2 shows species, where in the EVA experiments higher discrepancies occured, however in the ESQUIF-experiment the considered VOC species are in good agreement (up to a factor of 2). Larger ratios between modelled and measured ambient air concentrations have been found in the EVA experiment, especially for the components *n*-decane und n-nonane caused mainly by the use of white spirits as solvents. The components propylbenzene and 1,3,5-trimethylbenzene originate partly from white spirits, but also from traffic activities. The reasons for this considerable discrepancies could not be explained until now. That means there are new validation experiments necessary especially for longer chain hydrocarbons and oxygenated VOC from anthropogenic sources. The atmospheric fate of this species are not completely known until now.

The differences above are caused as well from the estimation of the total NMVOC emissions as from the split, thus the split uncertainties are lower. Furthermore, the split for combustion seems to be less uncertain than the split for solvent use.

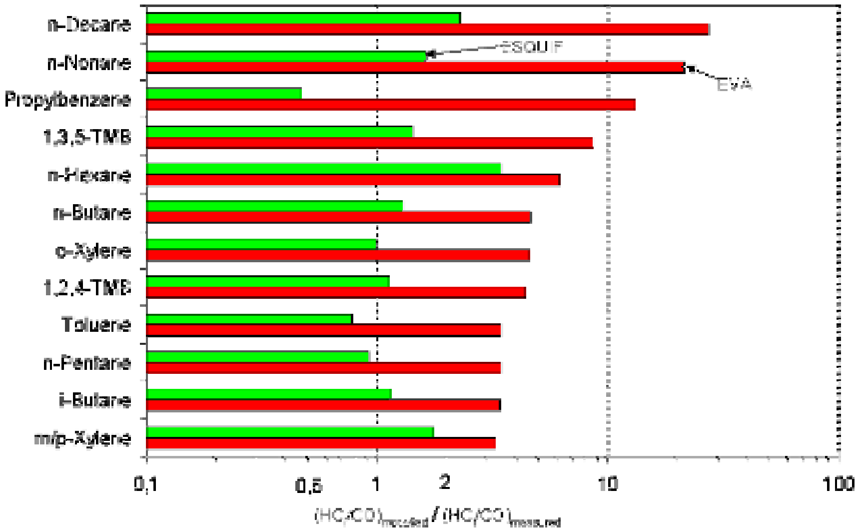

Figure 2. Results of the City experiments in Augsburg, Germany (EVA), [Kühlwein *et al.* 2002] and Paris, France (ESQUIF), [Vautard *et al.* 2003].

Ozone sensitivity calculations with a chemistry transport model

Initial point is the question where to find the major causes for uncertainties in the results in a complex emission model embedded in a system of models of emission simulation, dispersion, transformation, concentration and deposition. Since chemistry transport models issue a large amount of data, it is necessary to determine one or more target values for which uncertainties shall be investigated. Within the frame of this analysis, ozone is employed as a target value since it is a core element both in prevailing political discussion on air pollution and in tropospheric research.

The experimental set-up is illustrated in Figure 3 [Wickert, 2001; Wickert *et al.* 2004]. The lines drawn through indicate the part of the model usually realised in model-based air quality studies, with evaluation of concentrations of other air pollutants and meteorological fields being natural in this studies. The used CTM was the EURAD model.

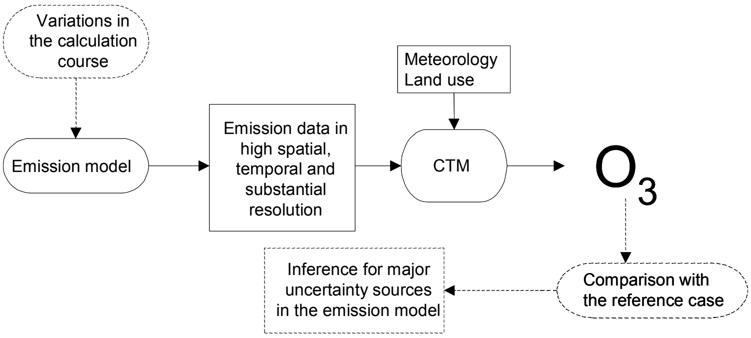

Figure 3. Schematic illustration of the sensitivity calculations.

The emission calculation model is variegated in a most diverse manner for the sensitivity calculation. The modified ozone concentrations are compared to the reference case, resulting from an execution of the model with most accurate emissions (dashed lines in Figure 3). This comparison allows a categorisation of the sub-models, according to their relevance on emission data quality.

The lines drawn through indicate basic ozone modelling with emission model and CTM, the dashed lines indicate additional steps for the sensitivity calculations.

Each of the large-scale areas determines the boundary values for the areas in high spatial resolution. The largest area (*Nest1*) contains Germany, Switzerland, Austria, The Netherlands, Denmark and parts of Poland, the Czech Republic, Slovakia, Hungary, Slovenia, Italy, France and Sweden with a grid width of 18 km and a total area of about 1.2 million km². The *Nest2* area (approximately 125,000 km²) comprises mostly the German *New Laender*, parts of Poland and the Czech Republic with a grid width of 6km. The grid with the highest spatial resolution of 2 km × 2 km focuses on an area of approximately 24,000 km² covering Greater Berlin-Brandenburg. Boundary values for the *Nest1* model are derived from a large-scale European simulation and are implemented alike for all sensitivity cases.

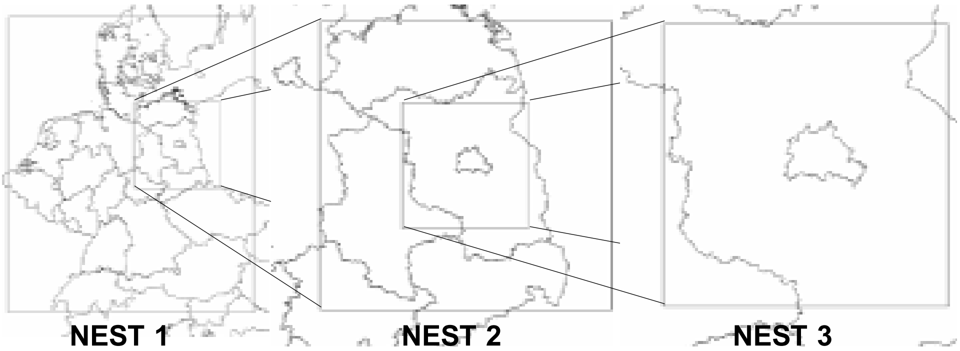

Figure 4. Areas of investigation for the sensitivity calculations. The large-scale areas provide boundary values for the areas with high spatial resolution.

"Switching off" the anthropogenic (OANT) or biogenic (OBIO) emissions can have different impacts on near-surface ozone concentrations. During the night, ozone is depleted by NO mostly emitted from traffic. As anthropogenic emissions in Germany are not included in the simulation, there are higher ozone concentrations in urban areas, at individual point sources or along highways in the OANT case than there are in the reference case. During daylight, in the photo-chemically active phase, anthropogenic emissions contribute to the formation of ozone. Thus, "switching off" these emissions leads to a reduction in ozone of 50µg/m³ compared to the reference case. Among other things, ozone precursors contribute to the formation of ozone. These precursors, that do not exist in the OANT case, were transported north-west due to corresponding meteorological conditions. In contrast, high ozone concentrations above the North Sea, as on 26th July, result from the transportation of a plume from the Netherlands due to westerly winds.

The lack of biogenous emissions (OBIO case) does not lead to such a dramatic concentration decrease as in the OANT case, but has similar tendency. During the night time, especially in areas without increasing ozone concentrations in the OANT case, exiguously increasing concentrations can be found. During daytime, there is less ozone produced, but the greatest difference is only minus 33 µg/m³.

In temporal course, the impacts of OANT and OBIO are different: In case of lacking of biogenic emissions, the greatest concentration decreases compared to the reference case can be found at dawn, while in the case without anthropogenic emissions, minima of the differences (= maxima of ozone reduction) can be found in the early afternoon and are much broader. Ozone increase at night, as from 25th July to 26th July, is in the OBIO case about twice as much as in the OANT case, presumably due to missing ozonolysis of the biogenic emitted substances.

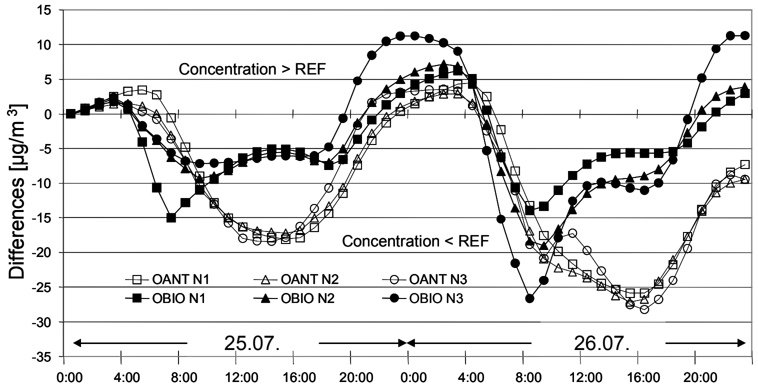

Figure 5. Differences in mean O_3-concentrations in the three nesting areas over time, comparing the reference case to OANT and OBIO – time stamps in UTC

The results displayed here, a large number of sensitivity calculations have been conducted to assess the uncertainties involved when running CTMs on the basis of high resolution emission data. Based on the comparison of concentration changes due to variations in emission inputs, far reaching conclusions could be achieved as to the relevant importance of influencing factors within the whole modelling system and regarding input data quantity and quality.

Anthropogenic as well as biogenic emissions have to be carefully modelled for the simulation of tropospheric ozone. In summer weather conditions during the investigated period, a high share of NMVOC emissions stems from biogenic sources, thus leading to a NO_x limitation of ground level ozone concentrations, *i.e.* ozone concentration changes occur typically due to changes in NO_x emissions. However, this cannot be averaged over the whole year, as only a quarter of annual NMVOC emissions are biogenic [Steinbrecher, 1999].

Regression analyses to determine correlations of concentration changes of ground level ozone with the uncertainty bands of anthropogenic resp. biogenic emissions lead to the conclusion, that errors (relative and absolute) in the modelling of biogenic emissions induce far larger deviations in ozone simulations, than errors in anthropogenic emissions. This is quite important as uncertainties of biogenic emissions are typically much higher than those related to anthropogenic emissions (up to a factor of 10 according to Guenther *et al.*, [2000]. On the other hand, errors in the emissions of anthropogenic NO_x emissions have a higher influence than errors in anthropogenic NMVOC emissions, which results in the recommendation to aim towards a as high as possible temporal and spatial resolution accuracy for the calculation of NO_x sources.

Not taking into account the plume super elevation of point sources can lead to a significantly greater error in the results than for instance a general over- or underestimation of NO_x emissions. Based upon this finding, the considerations of all major sources are modelled as point sources, in particular ozone simulations on small regional scale. In a similar way, taking into account the exact location of road transport emissions based on road networks improves the emission modelling results significantly.

The incorporation of land-use data to improve the spatial resolution of area source emissions seems to only increase the quality of emission date to a minor extent, as long as large point sources are accurately covered as individual sources.

Future outlook

To increase the representativeness of the aforementioned conclusions, further investigations should be conducted in a similar way. These should include, among other aspects, evaluations with other CTMs and evaluations of other regions and episodes with the same model. As the investigations providing the basis for this analysis have been conducted in an area with strong NO_x limitation due to dominating biogenic NMVOC contributions to ozone formation, further experiments should include NMVOC limited areas, as well as episodes with lower temperatures and thus less biogenic emissions.

In addition to that, it would be favourable to conduct similar exercises on a regional scale for other regions in Europe, provided a sufficient level of detail. This could be accompanied by scenario calculations to assess the importance of individual components of emission calculation models on future emission levels. The relevance of land-use data for the improvement of the spatial resolution should definitely be investigated more thoroughly.

As indicated above, specific attention should be devoted to the modelling of biogenic emissions, as they have a very high impact on ozone formation in particular during summer smog episodes, when they can exceed anthropogenic emissions of NMVOC by far. This has an impact not only on the absolute concentrations, but as well on the inherent uncertainty of the overall modelling system, especially with anthropogenic NMVOC emissions decreasing due to emission control activities.

The improvement of the knowledge of the atmospheric fate of longer chain hydrocarbons as well as oxygenated VOC is also needed.

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Synergistic Use of Satellite Retrievals, Ground-based Measurements and Modelling Studies Highlights Volatile Organic Compounds Fate in the Troposphere

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Motivation

The degradation of Volatile Organic Compounds (VOCs) is directly attached to the quality of life and human's health. This is due to their contribution to the photochemical smog, ozone changes and Secondary Organic Aerosol formation (SOA). In order to evaluate the potential impacts from both biogenic and anthropogenic VOCs, it is essential to better understand the processes that determine VOC oxidation in the atmosphere. Due to the large number of VOCs present in the atmosphere, understanding their atmospheric fate requires the determination of the spatial and temporal variation of selected VOCs that can be used as "proxy" for specific VOC categories (for instance anthropogenic or biogenic VOC) and the link of these VOC tracers with bulk VOC emissions and their fate in the troposphere.

This can be achieved by synergistic use of three different tools.

i) satellite retrievals of formaldehyde (HCHO) from GOME (Global Ozone Monitoring Experiment) and Glyoxal (CHOCHO) from SCIAMACHY (Scanning Imaging Absorption Spectrometer for Atmospheric Chartography) can be combined with

ii) ground based field measurements of peroxy radical species (ROx) conducted by the peroxy chemical amplification technique (PERCA) and supported by supplementary measurements of chemical species and meteorological parameters, and

iii) state-of the-art 0-D and 3-D chemistry-transport model simulations.

Introduction

Volatile organic compounds (VOC) have a number of anthropogenic sources mainly related to vehicle emissions, fuel and biomass burning, industrial activities, solvent usage and oil refining. In addition to human activities, the release of VOC by natural sources like vegetation and seawater is important. On a global scale, the biogenic organic compounds (BVOC) overwhelm the anthropogenic ones by a factor of 10-13 [Williams, 2004]. It is calculated that about 1300 $Tg\cdot y^{-1}$ are annually emitted into the atmosphere in the form of BVOC such as isoprene, terpenes and oxygenated organic compounds. In comparison, human induced sources emit approximately 100 $Tg\cdot y^{-1}$ [Williams, 2004]. Although over the last decade an increasing effort has been made to specify and quantify the VOC species present in the atmosphere, drastic progress is impeded by the large number of these species and their high spatial and temporal variation.

Once emitted to the atmosphere VOC species are removed via gas-phase reactions with radicals like hydroxyl (OH), nitrate (NO_3), halogen and halogen oxides and compounds like ozone. Peroxy radicals (ROx) are produced as short-lived intermediates in oxidation cycles of all natural and anthropogenic volatile organics. The final products of VOCs oxidation are formaldehyde (HCHO), glyoxal (CHOCHO) and ultimately carbon monoxide (CO).

Formaldehyde, the smallest aldehyde in the atmosphere is mainly formed through the oxidation of methane and other VOC by OH (Finlayson-Pitts and Pitts, 1986) but also from biomass burning and fossil fuel combustion. Glyoxal, the smallest a-a-dicarbonyl, is also formed mainly during the OH initiated oxidation of VOC. Both carbonyls are produced during anthropogenic as well as biogenic VOC oxidation. Recently, Volkamer *et al.* [2005] using LP-DOAS measurements demonstrated the robustness of results based on using both glyoxal and formaldehyde as proxies for VOC. In addition, glyoxal is involved in cloud chemistry and its distribution could provide an indicator on aerosol formation.

Approach and first results

In order to quantify the contribution of these two species, and consequently the role of VOC released by anthropogenic and biogenic activities, two different satellite-based spectrometers *GOME* (http://www.iup.uni-bremen.de/gome) and SCIAMACHY (http://www.iup.uni-bremen.de/sciamachy)*,* will be used. These instruments measure light scattered by the earth's atmosphere in the ultraviolet (UV) and visible (VIS) range. In these regions several trace gases were detected in the past [Burrows *et al.,* 1999; Richter *et al.,* 2002; Ladstätter-Weißenmayer *et al.*, 2003; Buchwitz *et al.*, 2005; Richter *et al.,* 2005, Wittrock *et al.*, 2006]. The satellite observations are compared for both species, HCHO and CHOCHO, with the results of a 3D CTM that is providing the link between the bulk VOC emissions and HCHO and CHOCHO columns. The first comparisons indicate the different behavior of HCHO and CHOCHO and in particular the link of glyoxal with aqueous phase chemistry.

Ground based measurements of peroxy radicals were conducted at the Finokalia observatory of the University of Crete, 70 km eastwards of Heraklion city, on Crete, Greece [Vrekoussis *et al,* in preparation]. During the same period a suite of other chemical parameters such as O_3, NO_y, CO, VOCs (mainly isoprene) and radon, photo-dissociation constants ($J(O^1D)$, $J(NO_2)$) and meteorological parameters (T, RH, wind speed and direction and solar irradiance) were also recorded facilitating the estimate and understanding of peroxy radical's behavior on a monthly and seasonal basis. Similar RO_2 observations have been reported for UK [Fleming *et al,* 2006].

These observations analyzed by comparison with a chemical box model [Vrekoussis *et al,* 2004] and a 3-D chemical-transport model [Tsigaridis and Kanakidou, 2003; Tsigaridis *et al.*, 2006] driven by ECMWF meteorology can provide insights in the accuracy of the chemical schemes and in particular with regard to the homogeneous and heterogeneous reactions taken into account.

Current and future outlook

The first stage of the current study already provided an extended time series of peroxy radicals and one of the few comparing to relevant studies [Zanis *et al*, 2003, Fleming *et al*, 2006]. In the short-term future, this study involves the development of the code of the models in order to better characterize the chemical processes taking place into the atmosphere. In addition, development of the fitting procedures also will take place concerning the glyoxal and formaldehyde retrievals from SCIAMACHY and GOME instruments respectively. The outcome of this synergistic study will add important information concerning the validation of the system ROx models, HCHO models, CHOCHO models and will serve as a proxy of characterizing areas with different chemical identity due to anthropogenic and biogenic activities.

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

10. Contributions from the Participants in Group 2

Modelling VOC Oxidation: Where does the Carbon go?

Contribution to the ACCENT workshop on Volatile Organic Compounds: Group 2

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Summary

The evaluation of the impacts of secondary organics on pollution episodes, climate, and the tropospheric oxidizing capacity requires modelling tools that track the identity and reactivity of organic carbon in the various stages down to the ultimate oxidation products, CO and CO_2. However, a fully detailed representation of the atmospheric transformations of these secondary organics involves a very large number of intermediate species, far in excess of the number that can be reasonably written manually. Here, we used a data processing tool to generate the explicit gas-phase oxidation schemes of organic compounds under tropospheric conditions. Simulations using these fully explicit oxidation schemes were performed to describe the gradual change of organic carbon during the oxidation of a given parent compound (here octane). Comparisons with the MCM chemical scheme were also performed.

Introduction

Volatile organic compounds (VOCs) emitted in the atmosphere are oxidized in complex reaction sequences that produce a myriad of intermediates. These intermediates play a key role in tropospheric chemistry:

(i) they are directly involved in the production of ozone and in the HOx and NOx budgets on regional and global scales;

(ii) they lead to the production of secondary organic aerosol (SOA) by nucleation and/or condensation on pre-existing aerosols and/or polymerisation; and

(iii) they are water soluble and interact with aqueous chemistry of radical, non metal and metal ions and oxidant pools during cloud events. These processes involving organic intermediates may have significant effects on atmospheric reactivity, composition, and radiative budgets on wide-ranging geographic scales. However, the magnitude of these effects remains poorly understood, due largely to a critical lack of information concerning the detailed composition of the highly functionalised secondary organics in the gas and condensed phases.

The development of explicit chemical schemes is necessary to test our current understanding of the evolution and impact of organic carbon during its atmospheric oxidation. However, the myriad of intermediates involved preclude any attempt to describe the numerous physical and chemical transformations manually (see Figure 1). Data processing tools are required to: (1) assimilate the various experimental data provided by laboratory studies, (2) codify the various estimation methods, and (3) generate consistent and comprehensive oxidation schemes on a systematic basis.

We used a "self-generating approach" to develop fully explicit gas-phase oxidation schemes of organic compounds under general tropospheric conditions. We present some results showing the major chemical characteristics of organic carbon during the oxidation of a given parent compound (here octane) and the potential benefit of using such an explicit scheme. In addition, some comparisons were made with the master chemical mechanism (MCM-v3.1) developed at the University of Leeds [Saunders *et al.*, 2003, Jenkin *et al.*, 2003] which is, to our knowledge, the most detailed scheme available in the literature.

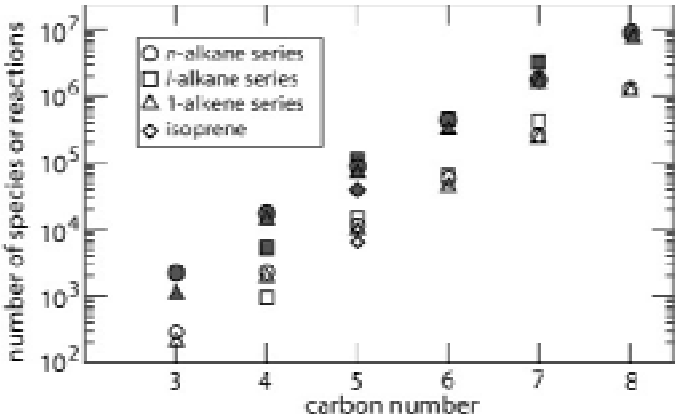

Figure 1. Number of products (open symbols) and reactions (grey symbols) created by the generator for various reactants.

The self generating approach

Explicit gas-phase oxidation schemes are written using the self-generating approach developed by Aumont *et al.* [2005]. This expert system is based on two main elements:

* a protocol defining a set of rules that lay out the choice of reaction pathways and provide the rate coefficients needed in the mechanism. When available, kinetic data taken from laboratory measurements are assigned to pathways. Otherwise, an estimation of the rate constant, stoichiometric coefficients and reaction products is performed using structure/activity relationships; and
* a generator which is a computer program that automatically creates the fully-explicit degradation scheme up to CO and CO_2 of a set of parent species provided as input on the basis of the predefined protocol.

The protocol and the main running stages of the generator are described in detail in Aumont *et al.* [2005]. Only salient points are summarised here. The development of “self-generated” chemical schemes requires the identification of all the reactions for each emitted organic compound and for their reaction products. These reactions generally include: (i) initiation of atmospheric degradation by attack with OH, NO_3, O_3 or photolysis, leading to the formation of peroxy radicals, (ii) reactions of peroxy radicals with NO, NO_2, NO_3, HO_2 and with other RO_2 radicals leading to the formation of stable reaction intermediates or alkoxy radicals RO and (iii) alkoxy radical reactions with O_2, unimolecular decomposition or isomerisation leading to the formation of stable reaction intermediates or new peroxy radicals. The possible functional groups produced during the oxidation of parent compounds are ketones, aldehydes, alcohols, hydroperoxides, nitrates, peroxy radicals, alkoxy radicals, carboxylic acids, peracids, peroxyacylnitrates and peroxyacyl radicals.

Organic budgets during gas-phase oxidation

Simulations were performed to examine the oxidation pathways of a given VOC. We present here some results obtained for the case of n-octane with a particular focus on the gradual change of organic compounds during oxidation.

The self generated master mechanism (SGMM) for octane (1.2×10^6 species and 7.9×10^6 reactions) and the MCM were implanted in turn in the same box model. The same set of inorganic reactions and the same photolysis frequencies were implemented in each scheme, so that differences could only be ascribed to the various organic schemes. Photolysis frequencies were computed for mid-latitude equinox conditions using the TUV model [Madronich *et al.*, 1998]. Time integration was performed using the two-step solver developed by Verwer *et al.* [1996]. Initial mixing ratios were respectively set to 10, 20 and 40 ppb for NOx, octane and ozone. With these conditions, the chemistry is characterized by a NOx saturated regime in the first day but a NOx limited regime on the remaining days.

Speciation of the primary carbon (*i.e.* octane), secondary organic carbon, and carbon monoxide is shown as a function of time in Figure 2a. For the conditions used here, octane is removed in about 8 days. At that time, most of the carbon lies in the secondary organic fraction, which is the dominant fraction after 1.5 simulated days. Figure 2b shows the distribution of secondary organic species as a function of the chain length. The secondary organic fraction is shown to be dominated by species holding 8 carbon atoms during the first 6 days. The contribution of organics with shorter chain length (C_1 to C_7) increases with time, reaching a maximum value after 8 days (see Figure 2b). The carbon budgets obtained with the SGMM and MCM are in fairly good agreement.

Figure 2c gives additional insight into the distribution of secondary C_8 and shows how these species are distributed as a function of the number of functional groups borne by the molecules. The SGMM typically yields organic products with 2 or more functional groups, while MCM organic products are dominated by mono or bi-functional species. These discrepancies are likely due to the fact that even a large mechanism like MCM (i) neglects many reaction pathways that individually make only a minor contribution and (ii) performs some lumping to represent secondary species using surrogates. This discrepancy in the representation of the substitution degree of the product carbon may lead to large differences in the estimated solubility and volatility of secondary organics.

Henry's law coefficients for many organic compounds were summarised by Sander [1999]. Available data shows that the Henry's law coefficients for most difunctional species typically lie in the range 10^2-10^5 $M.atm^{-1}$ (or higher for more than 2 functional groups). For a typical liquid water content of $L = 1$ $g.m^{-3}$ in clouds, species in that range can be classified as moderately to very soluble, *i.e.* dissolving significantly to almost totally in cloud droplets at thermodynamical equilibrium. These results thus strongly suggest that a significant fraction of the secondary organic carbon would dissolve into water droplets during cloud events.

Furthermore, SGMM results show that a non-negligible fraction of C_8 organics bear at least 4 functional groups (6 % of the secondary C_8 species, see Fig. 2c). Vapour pressure estimates using the Myrdal *et al.* [1997] group contribution method lead to extremely low vapour pressure for these kinds of species, typically in the range of 10^{-10} to 10^{-7} atm [Camredon *et al.*, 2006]. These compounds may thus be candidates for the formation of Secondary Organic Aerosols (SOA). The SOA mass was computed assuming simple gas/particle equilibrium, based on Raoult's law. For the simulation conditions used here, the SOA mass reached a maximum of 1.9 µg m^{-3} after 7 days. No organic condensation was obtained with the MCM.

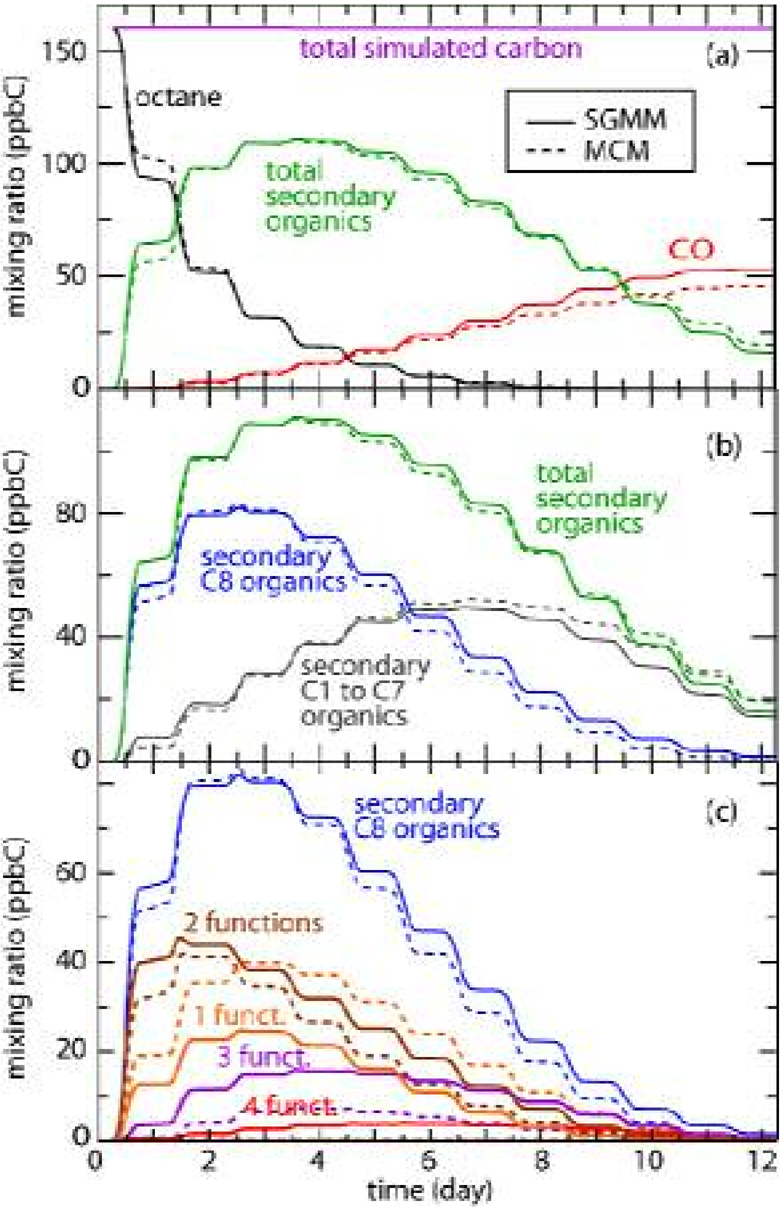

Figure 2. Evolution of carbonaceous species during the oxidation of n-octane. (a): distribution of the carbon; (b): distribution of secondary organic carbon for various chain lengths; (c): distribution of secondary C_8 organics as a function of the number of functional groups borne by the molecules. Solid lines are for the SGMM scheme, dashed lines are for the MCM scheme.

The distribution of the different organic moieties is shown as a function of time in Figure 3. The results are expressed as the ratio of the number of functional groups to carbon number ($R_{OF/C}$). Both mechanisms show similar behaviour. About 45 % of the organic carbon is found to be substituted at the end of the simulation. Some discrepancies are however found in the distribution of the functionalities. Terminal functionalities (*e.g.* -CO(OH), -CHO, -CO(OONO$_2$)) have a larger contribution in the MCM compared to the SGMM and vice versa for internal functionalities (*e.g.* ketone). Finally, the SGMM traps nitrogen into organic nitrate more effectively than does the

MCM (see Figure 3). As a result, the simulated NOx mixing ratio during the first 7 days is larger with the MCM than with the SGMM (see Figure 4a). These discrepancies in the nitrogen budget lead finally to a gap in the simulated O_3 mixing ratio (see Figure 4b), MCM simulations resulting in a less NOx limited regime than those performed with the SGMM.

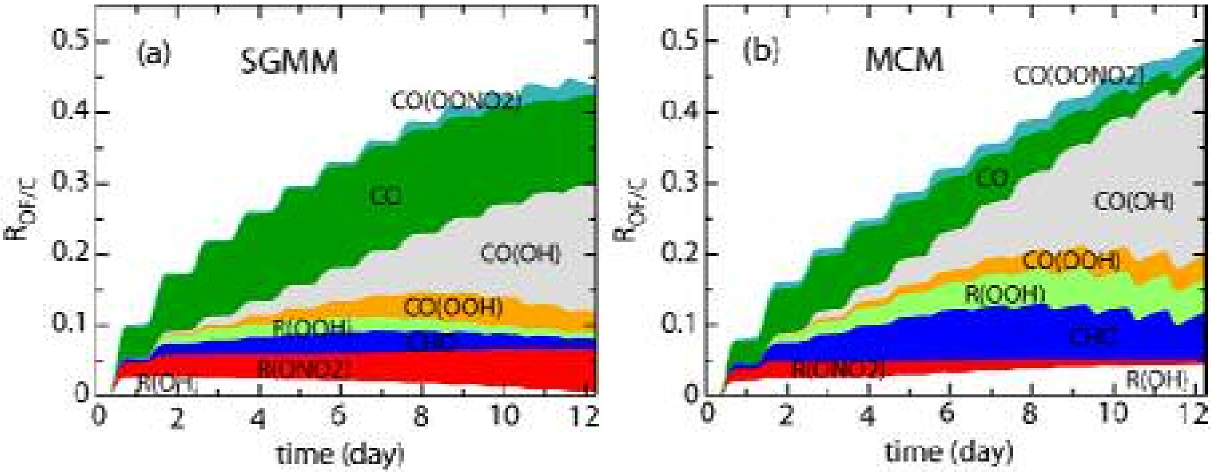

Figure 3. Evolution of the ratio of organic functionalities to carbon number during the oxidation of octane. (a): SGMM scheme; (b): MCM scheme.

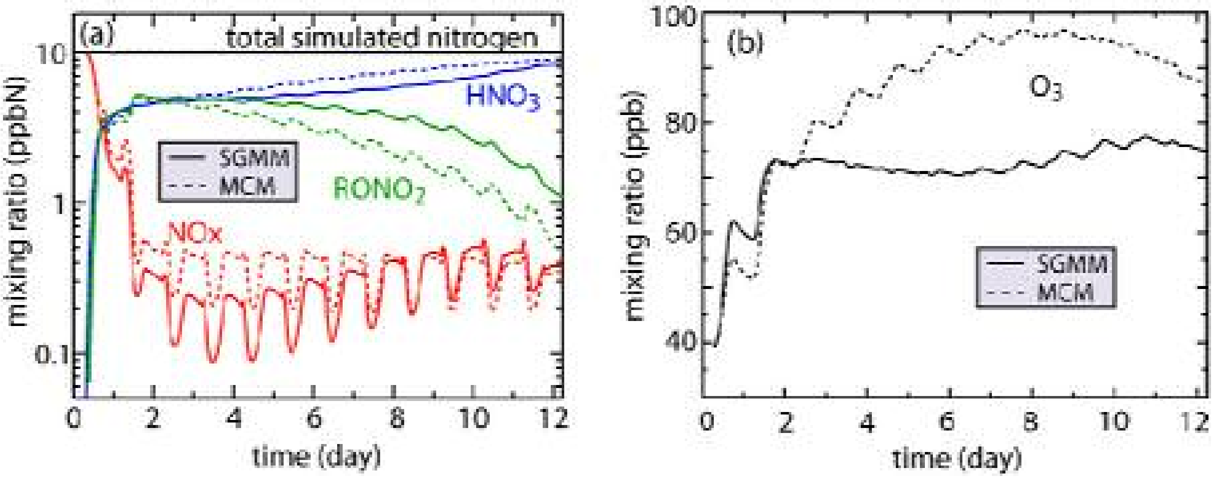

Figure 4. Evolution of nitrogen compounds (panel a) and ozone (panel b) during the oxidation of n-octane. Solid lines are for the SGMM scheme, dashed lines are for the MCM scheme.

Conclusions

Current chemical mechanisms neglect many reaction pathways and chemical species by assuming that they individually make only a minor contribution. We showed that their cumulative contribution could be important, especially with respect to the formation of highly functionalised species.

Many questions surround the role of multifunctional organic species in the chemistry of multiphase systems. The main difficulties lie in describing the sources and sinks of the myriad of VOC that may partition between the various condensed phases (aerosols and clouds). The SGMM generator is clearly a powerful tool to study this partitioning by its ability to explicitly describe the chemical dynamics of the various precursors. Extension of the self generating approach to model multiphase system would therefore provide a valuable exploratory tool to assess the role of condensed phases in the atmospheric evolution of organic compounds.

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On-line Measurement of Organic Acids in the Gas and Particle Phase with a WEDD/AC IC-MS

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Introduction

The sources of organic acids include direct emissions from anthropogenic and biogenic sources and secondary production via the photo-oxidation of volatile organic compounds (VOCs). Organic acids have been measured in the gas and particle phase as well as in wet precipitation in urban and rural areas. They increase the acidic load of the atmosphere but may also promote chemical conversions in the aerosols. Studies have shown that SOA produced in the presence of an acidic seed aerosol have higher yields compared to SOA formed in the presence of a non-acidic seed [Czoschke *et al.,* 2003; Iinuma *et al.,* 2004]. Oligomerization within SOA has recently been detected in the presence of acidic and neutral seed particles as well as in their absence [Gao *et al.,* 2004a, 2004b; Hoffmann *et al.,* 2002; Iinuma *et al.*, 2004; Tolocka *et al.*, 2004; Ziemann, 2002; Kalberer *et al.,* 2004] It has been rationalized that acid catalyzed reactions may promote the formation of oligomers. Surrat *et al* [2006] have shown the formation of polyesters in the SOA from isoprene photo oxidation.

Despite their importance in atmospheric chemistry, sampling of organic acids has been a challenge because of their semi-volatile behavior. Filter sampling is the most widely used sampling method, however, it cannot provide high time resolution data and has a drawback due to the positive and negative artifacts associated with it. In addition measurements that provide both gas and aerosol data of the organic acids during the same period of time are very scarce. To understand the diurnal and seasonal variations of organic acids in the gas and aerosol phase we use an online quasi continuous sampling and analysis method.

Scientific activities

To measure on-line organic acids in the gas and particle phase we use a wet effluent diffusion denuder aerosol collector (WEDD/AC) which is coupled to an ion-chromatograph. Detection of the ions occurs by a conductivity detector and a mass spectrometer. Mass spectrometry helps to identify organic acids present in the gas and particle phase which otherwise could not be identified with IC and conductivity detection alone. The WEDD/AC system can measure with a time resolution of 30-45 min allowing us to investigate the diurnal cycles and photochemical processes. The simultaneous measurement of gas and particle phase helps to elucidate the gas/particle partitioning of organic acids. Measurements were performed in urban and rural environments during different seasons as well as on a smog chamber.

Scientific results and highlights

We show here measurements of organic acids in the gas and aerosol phase from Zurich city during August–September 2002 and March 2003 [Fisseha *et al.*, 2006]. During this study on-line experiment were performed without mass spectrometric detection. However, filter samples were measured by IC-MS.

Formic and acetic acid were the most abundant organic acids measured in the gas phase. Primary sources are most important for acetic acid. In summer months secondary sources are important for the formation of formic acid, whereas primary sources dominate in March. Oxalic acid was the dominant identified dicarboxylic acid in the aerosol, implying secondary production as the major source in winter and summer. The concentrations of the monocarboxylic acids in the aerosol phase were very low compared to the corresponding gas phase concentrations Oxalic acid was found mainly in the aerosol phase. Figure 1 shows the concentrations of the organic acids in relation to the inorganic gas phase acids and SO_2. In total, the organic acids accounted for 42 % of the total gas-phase acids, from which 66 % were contributed by acetic acid. However, with respect to the total acid loading (including the aerosol phase) the contribution of organic acids is less than 20 %.

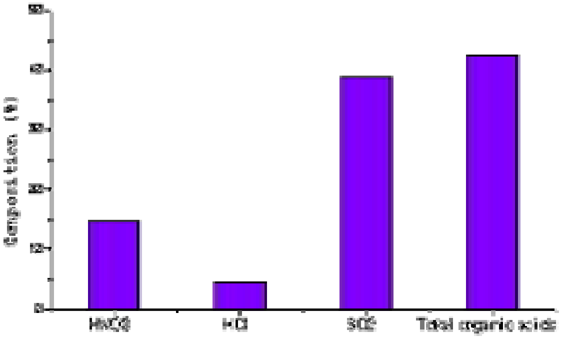

Figure 1. Contributions of the organic acids to the total acidity in the gas phase.

Filter samples were taken and off-line IC-MS measurements were performed. In total, 20 carboxylic acids were identified and quantified, of which 8 were monocarboxylic, 10 were dicarboxylic and 2 were tricarboxylic acids.

Most of the quantified carboxylic acids contained additional functional groups. Hydroxy-carboxylic acids were the most abundant classes of dicarboxylic acids next to aliphatic acids in the aerosol samples. Pyruvic acid was the only keto-acid identified. The MS enabled identification of compounds which could not be identified only from the IC measurements, because of their similar retention times. In addition, more than 20 unknown organic acids with m/z up to 249 were also detected with MS. Although one can infer the number of possible carboxylic groups from the retention time of the compounds in the IC, it was difficult to determine the structure of the compounds just from the retention time and the mass.

The sums of identified monocarboxylic, dicarboxylic and tricarboxylic acids accounted for 0.85–4.5 % (average 2 %) of WSOC (Figure 2). Unidentified masses are not accounted for this calculation, but could be as high as 7 % in total. The fraction of carboxylic acids during winter was in general lower than in summer particularly during February with high pollutant concentration.

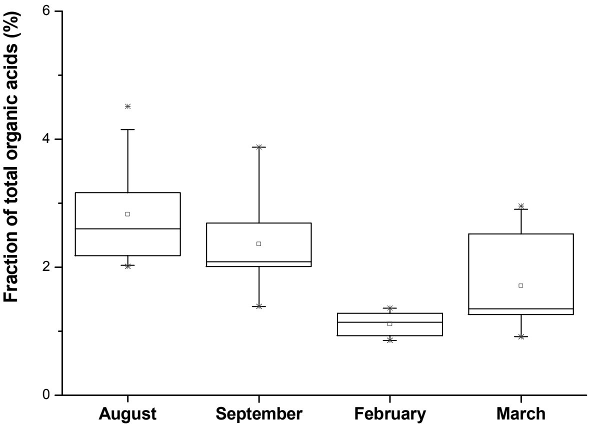

Figure 2. Fraction of the total organic acids in WSOC for the different months. The boxes indicate the median and the 25th and 75th percentiles, the open squares indicate the average, and the whiskers indicate the 1st and 99th percentiles.

Future outlook

Organic acids may play an important role in the oligomerization process in aerosols. This may be due to their role as acids but also as a reactant (esterification). Mass spectrometric detection led to the observation of many more organic acids in the samples which were not observed before with the conductivity detector alone. However identification of these acids must still be worked out. The sampling method may also suffer of artifacts. It has to be investigated if the hot steam used to collect the particle phase could produce acids by decomposition of labile species like peroxynitrates.

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Investigation of the Radical Product Channel of the $CH_3C(O)O_2 + HO_2$ Reaction in the Gas Phase

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Summary

The reaction of $CH_3C(O)O_2$ with HO_2 has been investigated at 296 K and 700 Torr using long path FTIR spectroscopy, during photolysis of $Cl_2/CH_3CHO/CH_3OH$/air mixtures. The branching ratio for the reaction channel forming $CH_3C(O)O$, OH and O_2 (reaction (1c)) has been determined from experiments in which OH radicals were scavenged by addition of benzene to the system, with the subsequent formation of phenol used as the primary diagnostic for OH radical formation. The dependence of the yield of phenol on benzene concentration was found to be consistent with its formation from the OH-initiated oxidation of benzene, thereby confirming the presence of OH radicals in the system. The dependence of the phenol yield on the initial peroxy radical precursor reagent concentration ratio, $[CH_3OH]_0/[CH_3CHO]_0$, is consistent with OH formation resulting from the reaction of $CH_3C(O)O_2$ with HO_2, such that the limiting yield of phenol at high benzene concentrations is well-correlated with that of $CH_3C(O)OOH$, a well-established product of the $CH_3C(O)O_2 + HO_2$ reaction (via channel (1a)). A value for the branching ratio, $k_{1c}/k_1 = (0.41 \pm 0.10)$, is derived, providing strong evidence for significant participation of the radical-forming channel of the reaction, in good agreement with the results of one previous study [Hasson *et al.*, 2004]. The implications of this result for atmospheric chemistry are briefly discussed.

Introduction

The reactions of organic peroxy radicals (RO_2) with HO_2 have long been recognised as chain terminating reactions which make a major contribution to controlling atmospheric free radical concentrations under NO_X-limited conditions [Jenkin and Clemitshaw, 2000]. Whereas radical termination via the near-exclusive formation of organic hydroperoxide products (ROOH) is well established for simple alkyl peroxy radicals such as CH_3O_2 and $C_2H_5O_2$ [Wallington, 1991; Hasson *et al.*, 2004], it has recently been recognised that selected oxygenated RO_2 radicals may possess significant radical-forming channels for their reactions with HO_2, thereby lessening their impact as chain terminating processes [Hasson *et al.,* 2004]. Of particular interest is the reaction of $CH_3C(O)O_2$ with HO_2. The $CH_3C(O)O_2$ radical is generated during the degradation of a large number of emitted volatile organic compounds $\geq C_2$, most notably isoprene (from a global point of view), and thus plays a major role in atmospheric chemistry.

The following product channels of its reaction with HO_2 have been identified [Niki *et al.*, 1985; Horie and Moortgat, 1992; Crawford *et al.*, 1999; Tomas *et al.,* 2001; Hasson *et al.*, 2004; Le Crane *et al.*, 2006]:

$$CH_3C(O)O_2 + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (1a)$$

$$\rightarrow CH_3C(O)OH + O_3 \quad (1b)$$

$$\rightarrow CH_3C(O)O + OH + O_2 \quad (1c)$$

Niki *et al.* [1985] first identified evidence for the participation of channels (1a) and (1b) from observation of the formation of $CH_3C(O)OOH$ and $CH_3C(O)OH$ in their FTIR product study, reporting a relative contribution of *ca.* 3:1 for the two channels, respectively. The significant participation of channel (1c) was first suggested in the FTIR/HPLC product study of Hasson *et al.* [2004], primarily to explain the formation of a significant yield of CH_3OOH (which can be generated from the subsequent chemistry of $CH_3C(O)O$) under conditions when $CH_3C(O)O_2$ is scavenged predominantly by HO_2. Accordingly, they reported a branching ratio of k_{1c}/k_1 = (0.4 ± 0.2). This conclusion has recently been challenged by Le Crane *et al.* [2006], who reported a re-evaluation of the results of the flash photolysis/UV absorption kinetics study of Tomas et al. (2001) from the same laboratory, and the results of new experiments in which benzene was added to the system to scavenge a proportion of any OH radicals generated. Based primarily on analysis of UV absorption traces at 290 nm (where the product hydroxycyclohexadienyl radical absorbs) Le Crane *et al.* [2006] reported an upper limit of $k_{1c}/k_1 < 0.1$.

In the present study, reaction (1) has been investigated at 296 K and 700 Torr using long path FTIR spectroscopy, during photolysis of $Cl_2/CH_3CHO/CH_3OH$/air mixtures, the same basic chemical system employed by both Hasson *et al.* [2004] and Le Crane *et al.* [2006]. Similarly to Le Crane *et al.* [2006], the formation of OH radicals in the system has been investigated by addition of benzene to scavenge variable proportions of OH, but with the subsequent formation of phenol used as the primary diagnostic for OH radical formation.

Experimental

All experiments were performed in the Ford 140 L Pyrex chamber, interfaced with a Mattson Sirius 100 FTIR spectrometer, which is described in detail elsewhere [Wallington and Japar, 1989]. The chamber is equipped with 22 fluorescent blacklamps (GE F40BLB), emitting near UV radiation in the range 300-450 nm. Radical generation was initiated by the photolysis of Cl_2, with $CH_3C(O)O_2$ and HO_2 radicals formed from the subsequent reaction of Cl atoms with CH_3CHO and CH_3OH, respectively, by the following well-established mechanisms:

$$Cl_2 + h\nu \rightarrow Cl + Cl \quad (2)$$

$$Cl + CH_3CHO \rightarrow CH_3CO + HCl \quad (3)$$

$$CH_3CO + O_2 (+M) \rightarrow CH_3C(O)O_2 (+M) \quad (4)$$

$$Cl + CH_3OH \rightarrow CH_2OH + HCl \quad (5)$$

$$CH_2OH + O_2 \rightarrow HCHO + HO_2 \quad (6)$$

Benzene was added to the reaction mixtures to scavenge variable proportions of OH radicals generated in the system. Benzene was selected because, unlike CH_3CHO and CH_3OH, it reacts slowly with Cl [$k = 1.3 \times 10^{-16}$ cm^3 $molecule^{-1}$ s^{-1}: Sokolov *et al.*, 1998], but comparatively rapidly with OH [$k_7 = 1.22 \times 10^{-12}$ cm^3 $molecule^{-1}$ s^{-1}: Calvert *et al.*, 2002]. The formation of phenol from the OH-initiated oxidation of benzene (reactions (7) and (8)) was used as the primary diagnostic for OH radical formation, the reported yield of phenol being (53.1 ± 6.6) % [Volkamer *et al.*, 2002]:

$$OH + C_6H_6\ (+M) \rightarrow HOC_6H_6\ (+M) \quad (7)$$

$$HOC_6H_6 + O_2 \rightarrow C_6H_5OH + HO_2 \quad (8)$$

Infra-red spectra of reagents and products were derived from 32 co-added interferograms with a spectral resolution of 0.25 cm^{-1}, and an analytical path length of 27.1 m. All experiments were carried out at 296 (± 2) K and 700 Torr total pressure of air.

Results and discussion

Reaction (1) was initially investigated in a series of experiments in which a high ratio of the peroxy radical precursor concentration, $[CH_3OH]_0/[CH_3CHO]_0 \approx 7$, was employed. Under these conditions, the production rate of HO_2 radicals is *ca.* 5 times greater than that of $CH_3C(O)O_2$ radicals, such that HO_2 radicals are in substantial excess. Previous studies [Niki *et al.,* 1985; Crawford *et al.*, 1999; Hasson *et al.*, 2004] have demonstrated that $CH_3C(O)O_2$ reacts exclusively with HO_2 under such conditions, and this was also confirmed in the present study from experiments carried out for a range of $[CH_3OH]_0/[CH_3CHO]_0$ ratios, as described further below.

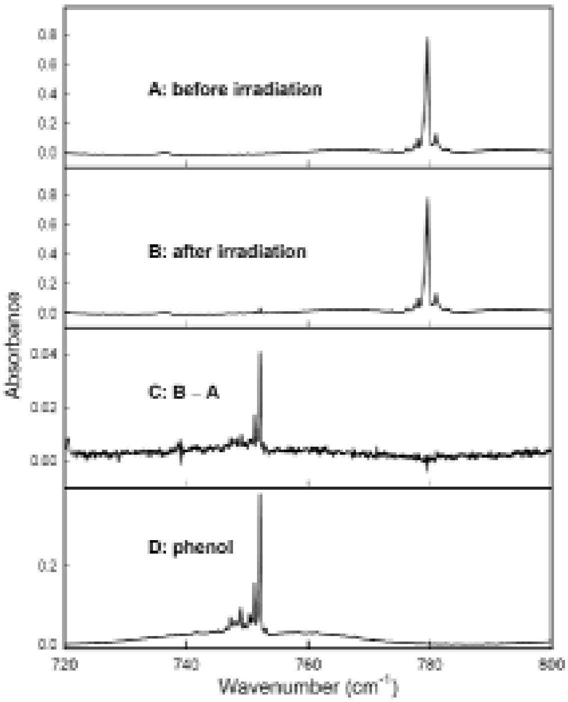

Figure 1. IR spectra obtained before (A) and after (B) a 55 sec irradiation of a mixture of 15 mTorr CH_3CHO, 100 mTorr CH_3OH, 1010 mTorr benzene, 100 mTorr Cl_2 in 700 Torr of air. The feature at 779 cm^{-1} is attributable to benzene. Panel C shows the difference spectrum. A reference spectrum of phenol is given in panel D.

Experiments were carried out with benzene present in the reaction mixtures at a series of pressures up to *ca.* 1 Torr. Owing to its extremely low reactivity with Cl, benzene at these pressures does not interfere with the production of $CH_3C(O)O_2$ and HO_2 under the conditions employed, scavenging ≤ 0.002 % of Cl atoms. However, it is sufficiently reactive with OH radicals to allow reaction (7) to compete with other reactions for OH, primarily with CH_3CHO and CH_3OH (reactions (9) and (10)),

$$OH + CH_3CHO \rightarrow CH_3CO + H_2O \tag{9}$$

$$OH + CH_3OH \rightarrow CH_2OH + H_2O \tag{10a}$$

$$\rightarrow CH_3O + H_2O \tag{10b}$$

leading to the formation of phenol by reaction sequence (7) and (8). Accordingly, phenol was observed in all experiments in which benzene was added, with the structured infra-red band near 750 cm^{-1} allowing it's sensitive and specific detection and quantification (see Figure 1). As shown in Figure 2 (inset), the yield of phenol relative to CH_3CHO consumed increased with benzene concentration in the system. To test that phenol formation was due to the OH-initiated oxidation of benzene (and not via some alternative oxidation mechanism), the yield of phenol (as determined from its initial formation rate, and corrected for its losses in the system) was plotted against the quantity $k_7[\text{benzene}]_0/(k_7[\text{benzene}]_0 + k_9[CH_3CHO]_0 + k_{10}[CH_3OH]_0)$. The resultant linear dependence (Figure 2) confirms that phenol formation indeed arises from reaction (7) occurring in competition with the other loss routes for OH, and therefore provides a clear demonstration that OH radicals are formed in the system. The plot also indicates that *ca.* 80 % of OH radicals were scavenged by reaction with benzene at the highest concentration employed (1 Torr), with the slope of the plot providing a measure of the limiting phenol yield under conditions when OH would react exclusively with benzene. This leads to a limiting phenol yield of (0.219 ± 0.016). Combining this value with the reported yield of phenol of (0.531 ± 0.066) from the OH-initiated oxidation of benzene [Volkamer *et al.*, 2002], provides a value of (0.41 ± 0.06) for the yield of OH radicals from the oxidation of CH_3CHO at high $[CH_3OH]_0/[CH_3CHO]_0$.

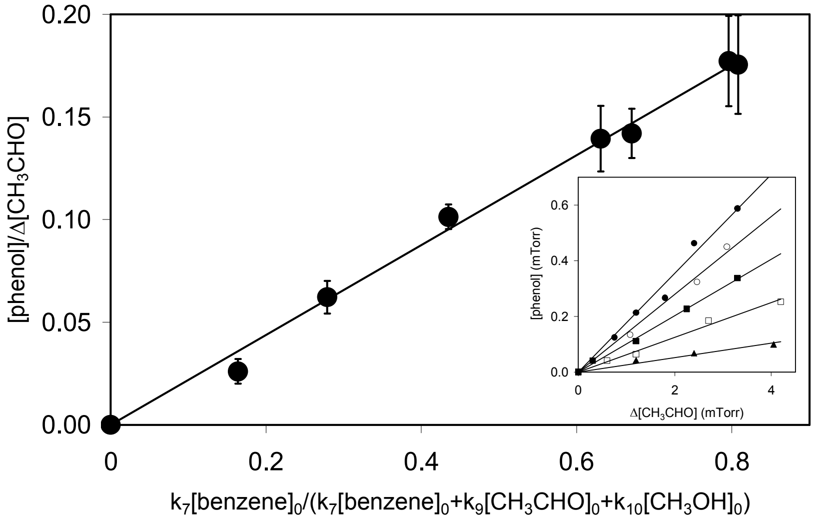

Figure 2. Observed yield of phenol vs. the calculated fraction of OH scavenged by reaction with benzene, in experiments with $[CH_3OH]_0/[CH_3CHO]_0 \approx 7$, with benzene added to the system at pressures up to *ca.* 1 Torr. Inset shows results for experiments with $[Cl_2]_0 \approx 100$ mTorr,$[CH_3OH]_0 \approx 100$ mTorr, $[CH_3CHO]_0 \approx 15$ mTorr, and with benzene at pressures of *ca.* 50 mTorr (triangles), 100 mTorr (open squares), 200 mTorr (closed squares), 450 mTorr (open circles) and 1 Torr (closed circles). Employed value of k_7 (= 1.22×10^{-12} cm^3 $molecule^{-1}$ s^{-1}) taken from the evaluation of Calvert *et al.* (2002), and those of k_9 (= 9.0×10^{-13} cm^3 $molecule^{-1}$ s^{-1}) and k_{10} (= 1.5×10^{-11} cm^3 $molecule^{-1}$ s^{-1}) from the evaluation of Atkinson *et al.* [2006].

To confirm that the production of OH results from reaction (1), the effect of varying the initial ratio of the peroxy radical precursors, $[CH_3OH]_0/[CH_3CHO]_0$, over the range zero to *ca.* 7 was also investigated, leading to a wide variation in the relative production rates of $CH_3C(O)O_2$ and HO_2. This series of experiments was carried out with benzene present at 1 Torr, to allow quantification of OH radical formation. In the absence of CH_3OH, there is no primary route to HO_2 formation, and $CH_3C(O)O_2$ radicals are initially removed by their self reaction:

$$CH_3C(O)O_2 + CH_3C(O)O_2 \rightarrow CH_3C(O)O + CH_3C(O)O + O_2 \qquad (11)$$

As described in detail elsewhere [Hasson *et al.*, 2004], the subsequent chemistry of the acetoxy radical, $CH_3C(O)O$, leads to the formation of CH_3O_2 radicals and HO_2 radicals, such that the "permutation" reactions of the three peroxy radicals occur in the system under steady state photolysis conditions. As a result, reaction (1) makes a reduced, but still significant, contribution to $CH_3C(O)O_2$ removal even when CH_3OH is absent.

Figure 3 shows the dependence of the limiting phenol yield (*i.e.* the OH formation diagnostic) on the precursor reagent concentration ratio. The yields remains approximately constant at *ca.* 0.22 from the high end of the range down to $[CH_3OH]_0/[CH_3CHO]_0 \approx 5$, but decrease at lower ratios to a value at zero $[CH_3OH]$ which is about one third of the high ratio limit. The relative dependence agrees well with that reported for $CH_3C(O)OOH$ previously by Crawford *et al.* (1999), based on experiments in the same chamber as used in the present study, indicating that the yields of $CH_3C(O)OOH$ and OH are well correlated for the complete range of conditions. Given that $CH_3C(O)OOH$ is a well-established product of the reaction of $CH_3C(O)O_2$ with HO_2 (reaction (1a)), with no other known sources in the system, the good correlation provides further support that OH radicals are generated by reaction (1c). Based on the above determination, therefore, we report a value of $k_{1c}/k_1 = (0.41 \pm 0.10)$, where the error limits are increased to allow for a 10 % contribution from possible systematic errors.

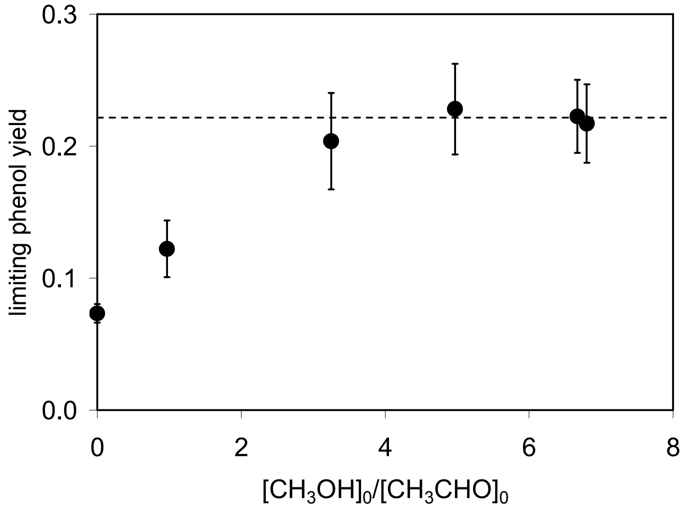

Figure 3. Variation of the high [benzene] limiting phenol yield (*i.e.* the OH formation diagnostic) with the peroxy radical precursor ratio $[CH_3OH]_0/[CH_3CHO]_0$.

These results thus provide strong evidence of a significant contribution from the radical-forming channel of the $CH_3C(O)O_2 + HO_2$ reaction. Although absolute confirmation would ideally require direct observation of OH formation, it is difficult to find an alternative explanation for the precise dependence of the phenol yield on the concentration of benzene and on $[CH_3OH]_0/[CH_3CHO]_0$. This conclusion therefore agrees with the branching ratio of $k_{1c}/k_1 = (0.4 \pm 0.2)$ reported by Hasson *et al.* [2004], but disagrees with the value of $k_{1c}/k_1 < 0.1$ reported by Le Crane *et al.* [2006]. Although Le Crane *et al.* [2006] employed a similar diagnostic for OH formation in their kinetics experiments (*i.e.* addition of benzene), it is noted that $CH_3C(O)O_2$ radicals are removed significantly by reaction (11) under the conditions employed (*i.e.* the system is less sensitive to reaction (1)), and that unambiguous observation of the formation of hydroxycyclohexadienyl radicals could be impeded by the formation and removal of a number of other absorbers at the monitoring wavelength of 290 nm.

Conclusions and atmospheric implications

The results presented above, and previously by Hasson *et al.* [2004], suggest that the reaction with HO_2 is a less efficient chain terminating process for selected oxygenated RO_2 radicals in the atmosphere than previously thought, which may alter our assessment of processes controlling ambient radical concentrations under NO_X-limited conditions. The results of Hasson *et al.* [2004] suggest that the reaction of $CH_3C(O)CH_2O_2$ with HO_2 has an even lower terminating fraction than reaction (1), and it is therefore possible that the reactions of HO_2 with acyl and α–carbonyl RO_2 radicals in general may be significantly propagating. It is therefore important that the possible participation of propagating channels is investigated for these and other RO_2 radical classes, in particular the β–hydroxyperoxy radicals generated from reactions of OH with alkenes and dienes, most notably isoprene and monoterpenes. Direct detection of the radical products (*e.g.* OH), and studies as a function of temperature would also be valuable.

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Oxygenated VOC Database

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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A new chemical kinetics database of gas-phase reactions of oxygenated VOCs has been set up and put online by the Laboratoire de Combustion et Systemes Reactifs, LCSR-CNRS, Orleans (http://www.era-orleans.org/eradb). Data is available for reactions of saturated, unsaturated, aromatic, halogenated and nitrogen-containing oxygenates with OH, NO_3, O_3, Cl and Br.

This database provides a compilation of recent kinetic data on gas-phase reactions of oxygenated VOCs with OH, NO_3, O_3, Cl and Br

Figure 1. Website of the OVOCs database (http://www.era-orleans.org/eradb).

Relevant information is given for each compound (structure, smile code, CAS, and other names). For each reaction the experimental conditions (temperature, pressure, technique, …) are tabulated along with the references and rate coefficient expression. The database provides a compilation of kinetic data with no recommendation.

In the near future, effort will be made to include photolytic quantum yields and lifetimes (in collaboration with Dr. G. Moortgat) and a limited amount of mechanistic data. It is also planned that the development/extension of the OVOC database should be closely linked with the Master Chemical Mechanism and CODATA/IUPAC. The linking of the OVOC database development with these other kinetic databases would provide a useful way of bringing together the knowledge gained from laboratory/chamber studies in a way that could feed easily into atmospheric models, using the proposed new MCM tools for mechanism development and simulation of complex chemistry.

This OVOC database has been developed with the support of ACCENT, ETHER and EUROCHAMP. The panel members are H. Sidebottom, I. Barnes, G. Le Bras and A. Mellouki.

Global Long-Term Measurements of Volatile Organic Compounds (VOC) within the WMO Global Atmospheric Watch (GAW)

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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From 30th January to 1st February 2006, the Expert Workshop on Volatile Organic Compounds (VOC) was held in the World Meteorological Organisation headquarters in Geneva. The Workshop was organized to support the Reactive Gases component of the Global Atmospheric Watch (GAW) programme.

This Report, as a product of the Workshop, forms the basis of the GAW strategy of supporting VOC measurements. As such it contributes to the next Strategic Plan of GAW for the period 2008-2015. The organizing team was Stuart Penkett (Chair), Rainer Steinbrecher (rapporteur) and WMO Environment Division staff (Slobodan Nickovic and Len Barrie). Prof. Penkett is Chairman of the GAW Scientific Advisory Group for Reactive Gases and a Member of the WMO/CAS (Comission for Atmospheric Sciences) Joint Scientific Steering Committee on Environmental Pollution and Atmospheric Chemistry that advises the GAW programme. Dr Steinbrecher is head of the GAW World Calibration Centre for VOC supported by Germany. The Report is composed of contributions by the Workshop participants (See list in ANNEX B).

Reactive non-methane hydrocarbon compounds commonly referred to as VOC play an important role in the chemistry and therefore the oxidizing power of the atmosphere, which in turn affects climate, and air quality. VOC are emitted by the biosphere and in various forms of air pollution, such as motor vehicle exhaust *etc.* They are removed from the atmosphere primarily by reaction with the hydroxyl radical with co-production of CO_2 and H_2O and many intermediate products. They are responsible, together with NOx, for the photochemical formation of O_3 and other photo-oxidant pollutants including secondary organic aerosol. A complex mixture of several hundred VOC is emitted with half-lives ranging from several months in the case of C_2H_6, to hours for the most reactive ones, such as isoprene or anthropogenic olefins.

The main importance of VOCs is in the lower troposphere, especially over and downwind of populated areas. However several compounds have sufficiently long lifetimes to be transported into the background atmosphere where their presence is supplemented by local emissions from the biosphere both over land and over ocean. Only a few molecules, for example formaldehyde (CH_2O) have the potential to be observed by current or proposed satellite instruments. It is therefore important and timely to institute at selected ground-based sites and from aircraft platforms a long-term measurement programme of a subset of VOCs which are relevant to the aims of the GAW, and which can be measured simply and accurately with existing technology.

GAW has long been mandated by WMO Members to coordinate long-term global observations of atmospheric ozone, UV, greenhouse gases, aerosols, selected reactive gases and precipitation chemistry (Strategic Plan: 2001-2007, Report #142 and addendum #156) for each variable. It is the practice of GAW to take care of all aspects of the GAW measurement triangle depicted in the Figure 1. GAW is taking the lead for WMO in implementing the Integrated Global Atmospheric Chemistry Observations

(IGACO) strategy that specifically targets VOCs as a priority for attention (GAW report #159).

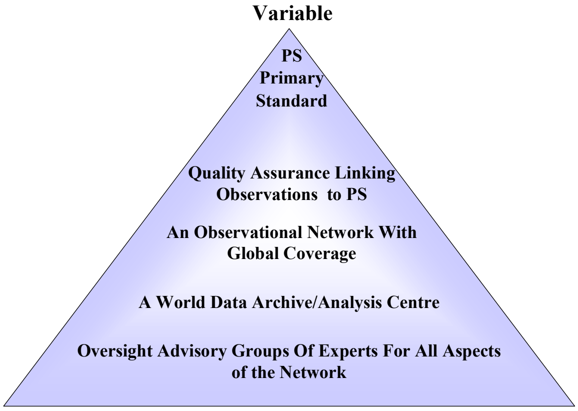

Figure 1. The GAW measurement triangle of necessary components of a global network.

VOC as a GAW component were previously considered in 1995 at the joint WMO-German Federal Research Ministry (GAW Report # 111).Presently world wide, there are some non-systematic VOC measurements scattered amongst a handful of laboratories and research institutions which are largely uncoordinated.

This 2006 Workshop at WMO in Geneva assembled a group of international experts representing the atmospheric chemistry observational research community (see list below). It involved first a selection of a target list of VOCs upon which GAW can focus. This report reflects the discussions of the experts and is made up of various sections concerned with the network, which will be set up to make VOC measurements in GAW. This will include flask networks measuring a limited number of molecules defined as core measurements and comprehensive measurement sites where an extended set of molecules will be made in addition to the core measurements (see Figure 2). The network section includes regular aircraft programmes making VOC measurements. Satellites with capabilities for making a global type of survey of the VOCs (including methane, formaldehyde) are listed in the IGACO report (IGACO, 2004). The satellite capability is limited to a few molecules, hence the need for a global network of ground-based stations supplemented by aircraft measurements.

The meeting spent some considerable time in a discussion of the core measurements, which could be made in the flask network. Molecules, as shown in Table 1 below, were chosen by criteria devised to determine their usefulness as tracers or aerosol precursors, and by their abundance in the background atmosphere and the feasibility of measurement in air stored in flasks of different types. The number of selected molecules is therefore much less than those defined in the earlier report (WMO No. 111) which focused more on molecules concerned primarily with regional air pollution. Rationale for inclusion of the target molecules will be elaborated in a separate section of this report.

The report also contains sections concerned with a GAW Central Calibration Laboratory, which will provide reference standards, and the World Calibration Centre, which will be responsible for ensuring that data collected within the network by whatever means, is intercalibrated. Finally, there is a section concerned with data archiving which will make use of the considerable expertise, which is available in the VOC measurement community.

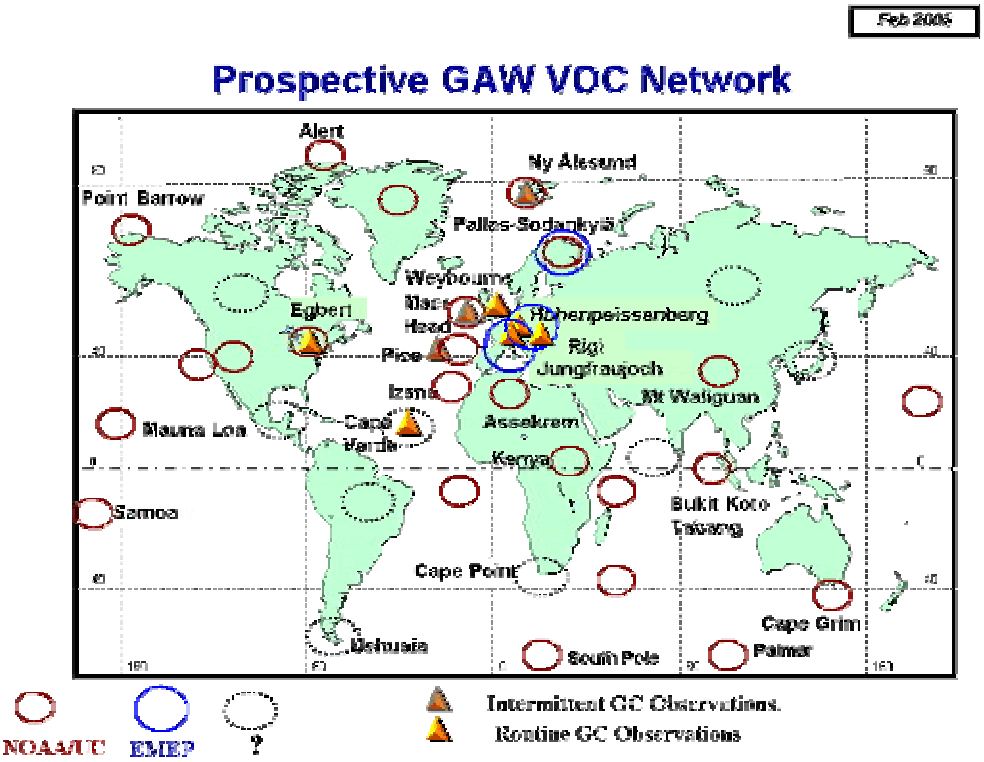

Figure 2. Proposed geographical distribution of the GAW VOC Network sites. Currently operating *in-situ* (GC) observatories are at Rigi and Hohenpeissenberg and Egbert. Continuous VOC monitoring at Weybourne, and Cape Verde is in the planning/preparation stage; the Mace Head and Mt Pico observatories have been operating intermittently. The circles indicate the desired distribution of flask sampling locations. Brown circles show the currently monitored sites within the NOAA/CU VOC programme. Blue circles indicate overlap with EMEP canister sampling sites. Dotted circles show desired locations that currently are not covered by any of the existing programmes.

Table 1. List of molecules for inclusion in the GAW VOC measurement suite with reasons for inclusion, measurement method and extent of network.

1.1 Molecule	1.2 Lifetime	1.3 Importance	1.4 Steel flask	1.5 Glass	1.6 Analysis	1.7 Network
Ethane	2-4 months	sources of methane natural sources biomass burning fossil fuel ocean production (S. hemisphere) trend in size for seasonal cycle indicator of halogen chemistry)	√	√	GC/FID	Global
Propane	3 weeks	source of methane natural sources biomass burning fossil fuel ocean production (S. hemisphere)	√	√	GC/FID	Global
Acetylene	3 weeks	motor vehicles biomass burning tracer ratios to the HCs trends	√	√	GC/FID	Global
Isoprene	1-2 hours	biosphere product sensitive to temperature/land use/climate change O_3 precursor Oxidizing capacity precursor to formaldehyde precursor to organic aerosol	?	?	GC/FID GCMS	Africa S and N. America Europe
Formaldehyde	2 hours to 2 days	indicator of isoprene oxidation biomass burning comparison with satellites trends	-	-	DOAS	Small no. of sites in Tropics for comparison with satellites
Terpenes	1 hour	precursors to organic aerosols	-	-	GCMS	
Acetonitrile	1 year	biomass burning biofuel burning?	-	?	GCMS	Global
Methanol	2 weeks	sources in the biosphere (methane oxidation) abundant oxidation product	-	?	FID PTRMS	Global
Ethanol	1 weeks	tracer of alternative fuel usage	-	?	FID PTRMS	Global
Acetone	1 month	abundant oxidation product free radical source in the upper troposphere	?	?	FID PTRMS	Global
DMS	1 day	major natural sulphur source sulfate aerosol/climate tracer of marine bioproductivity	?	?	FID PTRMS	Marine
Benzene	1 week	tracer of combustion biomass burning	√	?	FID GCMS	Global
Toluene	2 days	ratio to benzene used for air mass life time precursor to particulates	-	?	FID GCMS	Global
Iso/normal Butane	2-3 days	chemical processing indicato lifetime/ozone production	√	√	FID GCMS	Global
Iso/normal Pentane	2-3 days	ratio provides impact of NO_3 chemistry	√	√	FID GCMS	Global

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Evidence for Large Average Concentrations of the Nitrate Radical (NO_3) in Western Europe from the HANSA Hydrocarbon Database

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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The nitrate radical (NO_3) was first measured in the atmosphere in the 1970s and suggestions were made that it could play a major role in oxidising many unsaturated hydrocarbons, such as those emitted from the biosphere. Analysis of the hydrocarbon mix over the North Atlantic Ocean suggested subsequently that the influence of NO_3 radical chemistry at night was even more extensive, being on a par with hydroxyl radical chemistry at some times of the year.

The paper presents a detailed analysis of an extensive data base of many nonmethane hydrocarbons collected at various sites around the North Sea in the mid 1990s during the HANSA project. By comparing the relative rates of oxidation of *iso* and normal pentane with that of toluene and benzene it clearly shows that the efficiency of NO_3 radical chemistry and hydroxyl radical chemistry over northwest Europe are similar in springtime and predicts an average night-time NO_3 concentration of the order of 400 pptv, assuming an annual average OH concentration of 0.6×10^6 cm^{-3}. This value is very dependent on the average emission ratios of the different hydrocarbons and values between 250 and 600 pptv are possible. It is much larger than direct measurements made in Europe at the surface, but is of the same magnitude as concentrations measured recently from aircraft in the boundary layer over the northeast USA, and previously in vertical profiles by remote sounding over Europe.

A simple analytical expression can be derived to calculate the NO_3 concentration at night with the only variables being ozone and the loss rate of N_2O_5, either to the ground or to aerosol surfaces. The concentrations of NO_3 calculated in this manner are similar to those derived from the analysis of the HANSA hydrocarbon database for typical conditions expected over Europe, but they are very dependent on the efficiency of the aerosol sink for N_2O_5.

It is shown that NO_3 oxidation of many unsaturated hydrocarbons can indeed be more efficient than OH oxidation, especially at times of the year outside the summer season. Direct evidence for hydrocarbon oxidation by NO_3 radicals is shown by a series of peroxy radical measurements where the nighttime concentrations can be significantly higher than daytime concentrations in polluted air on occasion. Also the winter/summer (W/S) ratios of many unsaturated hydrocarbons are much lower than those expected from their removal purely by hydroxyl radical chemistry.

The consequences of these findings are profound especially as satellite measurements of NO_2, a major precursor to NO_3, suggest that these high average concentrations of several hundred pptv could be widespread over most of the continents. This needs to be confirmed by direct *in-situ* measurement of nitrate radicals but it suggests a much larger role for NO_3 chemistry in the oxidation capacity of the atmosphere than realised hitherto.

Reactivity of Unsaturated Oxygenated VOC with NO_3 Radical

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Summary

NO_3 oxidation of vinyl ethers and unsaturated esters has been studied under tropospheric conditions in the LISA indoor simulation chamber. Kinetic experiments were carried out by relative and absolute rate techniques. Kinetic results show that vinyl ethers are very reactive towards NO_3 and their night time lifetimes have been estimated to be smaller than few hours. Experiments on esters, which are still in progress, tend to indicate that unsaturated esters are much less reactive towards NO_3 radicals than vinyl ethers. From mechanistic study, main oxidation products were identified and quantified. Future experiments on biogenic oxygenated VOC will be carried out soon.

Introduction

Oxygenated volatile organic compounds are widely emitted into the troposphere by both anthropogenic (use as solvents in paints, pharmaceutical process synthesis, adhesives) and biogenic sources [Graedel *et al.,* 1986]. When released into the troposphere, they can undergo either photolysis or oxidation by OH and NO_3 radicals and by ozone. The nitrate radical is formed by reaction of NO_2 with ozone and has been observed and shown to be an important oxidant during night time. Since NO_3 is very efficiently photolysed in sunlight and reacts rapidly with NO which is a predominantly daytime species, it can not accumulate during the day. For this reason, its daytime reactivity was considered to be negligible for many years. But recently, Geyer *et al.*, [2003] and Brown *et al.*, [2005] have shown that for highly reactive VOC, NO_3-oxidation was not a negligible process during the day. For example, NO_3-oxidation of α-pinene in the presence of NOx contributes to 10-40 % of the total daytime oxidation rate.

Unsaturated oxygenated VOC, because of their unsaturation and the potential activation effect of oxygen are suspected to be very reactive. Hence, their reactivity with NO_3 may contribute significantly to their loss process, even during the day! For this reason, new kinetic and mechanistic experiments of NO_3-induced oxidation of unsaturated OVOC are needed.

Scientific activities

At LISA, the workgroup directed by J-F. Doussin is working on the reactivity of VOC towards atmospheric oxidants. In particular, NO_3-oxidation processes are studied for several years and recently, experiments have been performed on vinyl ethers and unsaturated esters which are widely emitted by anthropogenic sources. In particular, new “friendly” solvents including vinyl ethers are used to replace traditional ones. Hence, as vinyl ethers emissions may go increasingly, it appears necessary to study their reactivity in order to precisely evaluate their environmental impact. This study was supported by the European program MOST (Multiphase Chemistry of Oxygenated Species in the Troposphere).

Kinetic and mechanistic oxidation of four vinyl ethers R-COCH=CH_2 (methyl, ethyl, *n*-propyl and *n*-butyl) and unsaturated esters (vinyl acetate $CH_3C(O)OCH=CH_2$, isopropenyl acetate $CH_3C(O)OC(CH_3)=CH_2$ and allyl acetate $CH_3C(O)OCH_2CH=CH_2$) have been investigated under simulated atmospheric conditions (295 ± 3 K, atmospheric pressure). Experiments were performed in the atmospheric simulation chamber of LISA made of a Pyrex reactor (6 meters long, volume 977 litres). Analysis were performed using two *in-situ* spectrometric devices, a FTIR spectrometer and a UV-visible spectrometer, both coupled to multi-reflection White-cells (infrared path length: 156 m, UV-visible path length: 72 m). In particular, UV-visible spectrometry was used to monitor NO_3 concentrations during the experiments for absolute rate determinations.

Scientific results and highlights

For all investigated OVOC, rate constants were determined by relative rate technique and for some of them by both absolute and relative rate techniques. Obtained rate constants and deduced atmospheric lifetimes are presented in Table 1. It can be observed that vinyl ethers are very reactive towards NO_3 with estimated lifetimes smaller than few hours. As a consequence, the reactivity with NO_3 is a significant loss process of vinyl ethers. First results obtained for unsaturated esters indicate that these compounds are much less reactive with NO_3 radicals than vinyl ethers.

Table 1. Rate constants and calculated lifetimes of oxygenated VOC with respect to NO_3, OH and O_3. [a]: [Thiault and Mellouki, 2006]; [b]: [Grosjean and Williams, 1992]; [c]: [Ferrari *et al.*, 1996]; [d]: [Grosjean and Grosjean, 1998]

Compound	NO_3		OH		O_3	
	k (10^{-13} cm^3 $molec.^{-1}$ s^{-1})	Lifetime ([NO_3] = 10 ppt)	*k* (10^{-11} cm^3 $molec.^{-1}$ s^{-1})	Lifetime ([OH] = 2.10^6 $molec.cm^{-3}$)	*k* (10^{-16} cm^3 $molec.^{-1}$ s^{-1})	Lifetime ([O_3] = 50 ppb)
Methyl vinyl ether	7.2 ± 1.5	1.5 h	4.53 ± 0.70[a]	3 h	-	-
Ethyl vinyl ether	13.1 ± 2.7	50 min	7.24 ± 0.81[a]	2 h	1.95 ± 0.14[a]	1 h
Propyl vinyl ether	13.3 ± 3.0	50 min	10.5 ± 1.4[a]	1.5 h	2.35 ± 0.38[a]	1 h
Butyl vinyl ether	17.0 ± 3.7	40 min	11.1 ± 1.4[a]	1.5 h	2.85 ± 0.15[a]	1 h
Vinyl acetate	0.11 ± 0.01	4 days	4.9[b]	3 h	0.032 ± 0.005[d]	3 days
I-propenyl acetate	In progress	-	6.2 ± 0.1[c]	2 h	-	-
Allyl acetate	In progress	-	2.46 ± 0.03[c]	6 h	-	-

From analysis of infrared spectra, main oxidation products were identified and some were quantified (see example in Figure 1). For vinyl ethers, they are formaldehyde, formate (methyl, ethyl, propyl or butyl) and nitrates (including peroxynitrates). Yields of formaldehyde and formate were found to be ~ 50 %. Nitrates were not directly quantified but their contribution was estimated from the missing carbon to be ~ 50 %. These results have recently been published [Scarfogliero *et al.*, 2006].

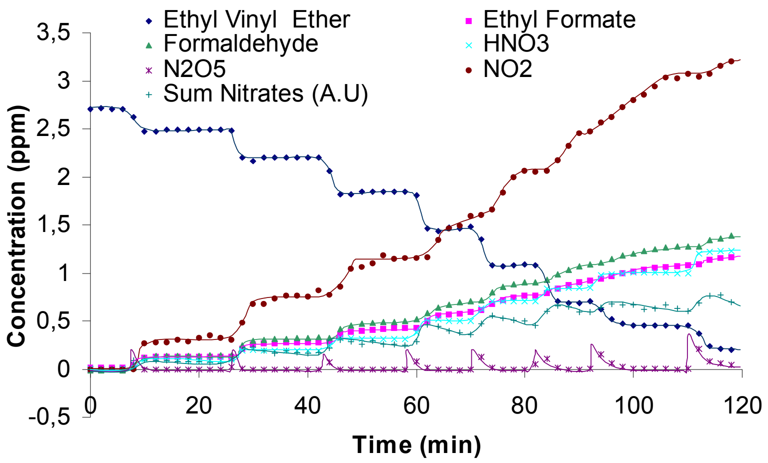

Figure 1. Plots of concentrations of reactants and products *vs*. time for NO_3 oxidation of ethyl vinyl ether.

Future outlook

Emissions of biogenic VOC (BVOC) greatly exceed those of anthropogenic ones and are estimated to be more than 1000 Tg/year on a global scale [Guenther *et al.*, 1995]. The biogenic VOC that are emitted are mainly isoprene and monoterpenes but a wide range of other compounds including oxygenated VOC are also emitted [Helmig *et al.*, 1999], [Kesselmeier and Staudt, 1999]. One important characteristic of many biogenic VOC is their high reactivity towards atmospheric oxidants since these molecules have one or several unsaturations. As already discussed, NO_3 oxidation of these highly reactive compounds can play a key role, even during the day. In particular, [Brown *et al.*, 2005] have shown that daytime NO_3 oxidation of monoterpenes, that produces partially organic nitrates (whereas OH-oxidation produces oxygenated species), may have implications for ozone formation. Hence, because each NO_3 contains two odd oxygens (*i.e.* oxidation of NO to NO_3 requires two O), loss of NO_3 to form organic nitrates effectively removes two ozone molecules for every NO_3 consumed.

Since oxygenated BVOC have been less studied than monoterpenes and are also suspected to be very reactive, it appears necessary to study their reactivity towards NO_3 in order to evaluate their implication in night time and daytime chemistry. In particular, we can wonder about the role played by the oxygenated BVOC on ozone budget. Among oxygenated BVOC, compounds such as unsaturated alcohols, esters and carbonyl compounds will be studied.

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VOC from Monitoring Networks: The GAW Station Hohenpeissenberg

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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VOC are measured as part of the Global Atmosphere Watch programme (GAW) at Hohenpeissenberg by two gas chromatographic systems: a GC-FID for the C_2-C_8 hydrocarbons [Plass-Dülmer *et al.*, 2002], and GC-FID/MS for C_5-C_{12} hydrocarbons including monoterpenes. Measurements are routinely made twice a day (1:00 and 13:00 CET), during intensive phases up to hourly. Here we demonstrate uncertainties, GAW objectives and usefulness of such monitoring series.

Uncertainties in VOC measurements – Intercomparison Exercises

Several international intercomparison activities have been carried out in recent years, *e.g.* NOMHICE, AMOHA, first GAW intercomparison. These are very useful to address the uncertainties of current VOC measurements. In order to evaluate the quality of results, ranking procedures have been introduced by defining measures based on the deviations of participants' results from reference concentrations. As an example, in Figure 1 results of the last phase of the AMOHA intercomparison, phase 4.2, are shown [Plass-Dülmer *et al.*, 2006]. This intercomparison exercise for the first time included a joined sampling of ambient air by participants, storage in canisters, and analysis, thus comprising the whole measurement process encountered in monitoring networks. The results show considerable scatter representing the results of 10 groups in 3 consecutive intercomparison phases. The horizontal bars show the data quality objectives defined by GAW, 10 % for alkanes, 15 % for aromatics, and 20 % for the alkenes, and 50 % for concentrations below 100 pptv. About 2/3 of the results were in line with the data quality objectives, which appears to be a promising result with respect to the encountered complex, whole air sample at low concentrations. A similar fraction of "good" results was obtained in the first GAW intercomparisons carried out by the world calibration centre (WCC) for VOC in Garmisch, Germany [Rappenglück *et al.,* 2006]. About halve of the participating laboratories achieved fairly "good" results. Strategy of GAW-VOC is that the WCC works on improving the quality of the VOC monitoring laboratories by performing station audits with focus on the weaker performing laboratories and further intercomparison exercises in future [WMO-GAW, in preparation].

Common calibration standards for VOC

The GAW VOC network aims at common calibration gas mixtures all over the globe in order to reduce uncertainties due to different calibration scales [WMO-GAW, in preparation]. Currently, GAW is in the process of negotiations with national metric institutions (NIST, NPL, NMI, KRISS…) to implement Central Calibration Laboratories (CCL). The CCL's are intended to provide VOC calibration gas mixtures at uncertainty levels of better than 3 % for C_2-C_7 hydrocarbons, and better than 5 % for oxygenated compounds and monoterpenes.

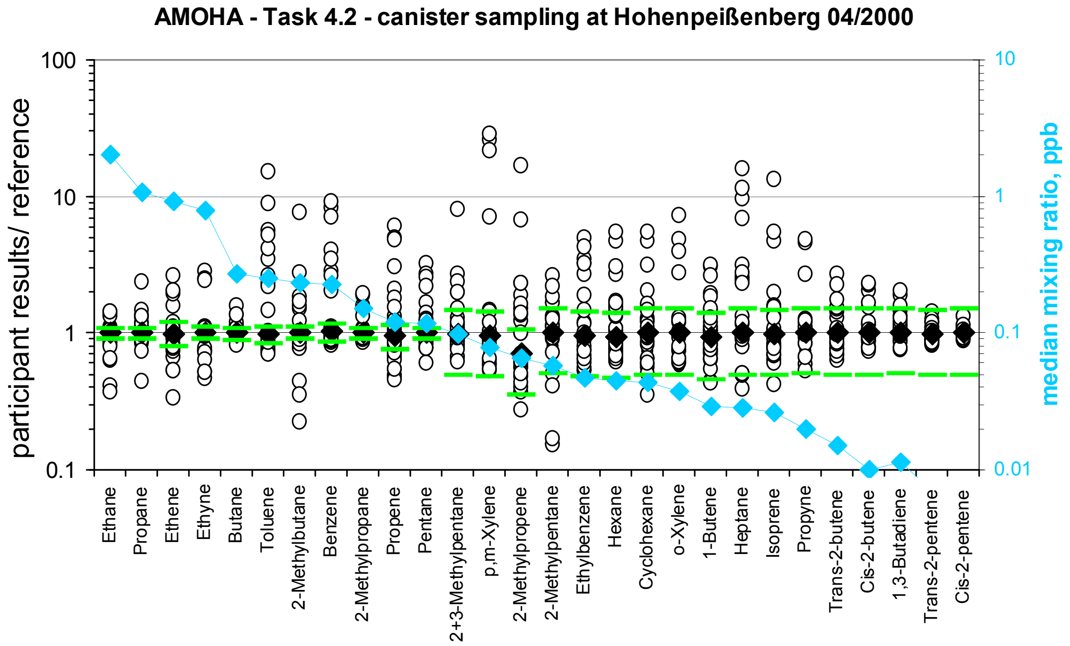

Figure 1. Results of AMOHA

Cross links between different monitoring concepts

Since 2005, Detlev Helmig's group (University of Colorado) analyses VOC in the rest gas from flasks of the carbon cycle group's cooperative global air sampling network by NOAA-ESRL. To assess the quality of thus determined VOC concentrations, at Hohenpeissenberg corresponding flask samples are routinely sampled simultaneously with our on-line measurements. A similar intercomparison is under way at Pallas (Finland) to get a link with the EMEP-VOC network.

Changes in atmospheric VOC composition

From the monitoring stations, global distributions and trends in VOC composition can be detected. Objective of the current VOC monitoring program is to detect changes in the composition of the atmosphere related to global climate change [WMO-GAW, 1995, in preparation]. This covers both, changing emission rates due to climate change of predominantly biogenically emitted compounds or biomass burning, and feedback to climate through ozone and aerosol formation. Such data sets are essential in evaluating models and emission inventories.

VOC turn-over rates with OH

The contributions of the various compounds to the turn-over rates with OH radicals at Hohenpeissenberg are shown in Figure 2.

In summer, biogenic VOC contribute about a third, all VOC about halve of the total turn-over. Anthropogenic VOC are of minor importance in summer, however, they comprise the dominant VOC in winter with about 20 % contribution to total turn-over. Those VOC with highest mixing ratios, *e.g.* long lived alkanes, aromatics and OVOC's, contribute fairly little to the local turn-over, underlining the important role of very reactive, mostly biogenic compounds on photo chemistry in rural, continental atmosphere.

These figures mainly include the primary turn-over of hydrocarbons, and by this do not appropriately cover contributions by corresponding reaction products (secondary VOC).

This may increase the turn-over rates due to all VOC substantially, possibly by factors of 2 to 3.

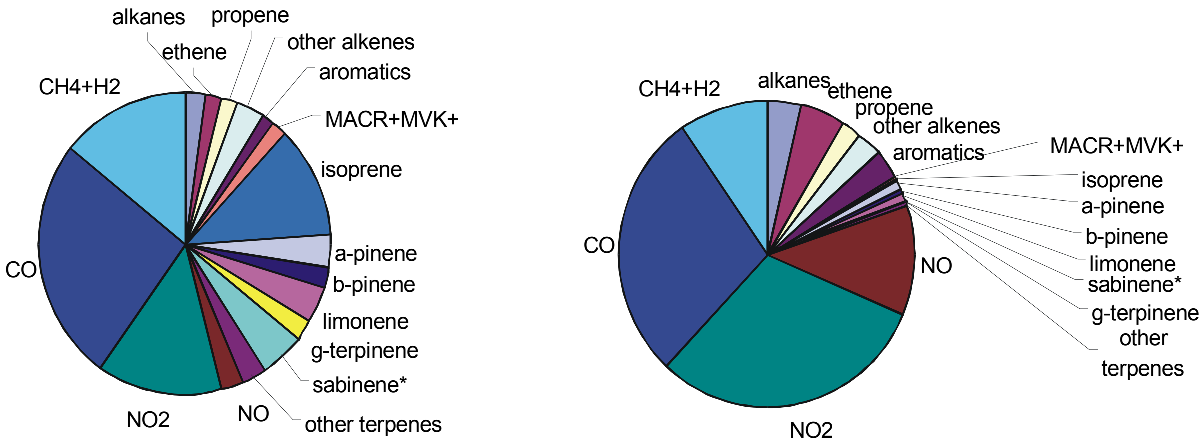

Figure 2. Turn-over rates due to reactions with OH radicals for the months Jun-Aug (left) and Dec-Feb, 2004 (right); noon time mixing ratios were used with concurrently measured OH concentrations to calculate turn-over rates; total turn–over is 10×10^6 molecules cm^{-3} s^{-1} in summer; and 3.5×10^6 molecules cm^{-3} s^{-1} in winter (sabinene*: corrected for instrumental artifact).

In a recent paper, Rohrer and Berrresheim [2006] have demonstrated a linear relation between the concentration of OH radicals and the ozone photolysis frequency $J(O^1D)$ (R = 0.941) at Hohenpeissenberg. This relationship proved to be robust for a period of 5 years including different seasons. Due to the large impact of VOC on this relationship at Hohenpeissenberg, such studies could be used to infer the contribution of VOC. Especially, based on measurements of comprehensive sets of VOC the role of secondary VOC could be addressed: how many oxidation cycles do they run through until they are removed from the gas phase and enter the particulate phase. This approach should be complemented by measurements of the total OH-reactivity.

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Uncertainties in the Mechanisms for the Atmospheric Oxidation of Aldehydes

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Summary

The mechanisms for the atmospheric degradation of small aldehydes (RCHO) are reasonably well known. However, recent experimental evidence suggests that alternative pathways are available to the intermediate acyl (RCO) and acyl oxy (RC(O)O) radicals, particularly when R is not a simple alkyl group. Acyl radicals may undergo prompt decomposition to produce R + CO, whilst large acyl oxy radicals could isomerize to produce carboxylic acids. Experimental and theoretical studies of these reactions need to be performed for a variety of functionalised aldehydes in order to determine their potential importance.

Introduction

Aldehydes are emitted directly into the atmosphere from a variety of natural and anthropogenic sources and are also formed *in situ* from the gas-phase degradation of volatile organic compounds. The atmospheric fate of aldehydes is controlled by photolysis and reaction with hydroxyl (OH) or nitrate (NO_3) radicals and, in the case of unsaturated compounds, reaction with ozone [Atkinson and Arey, 2003]. The currently accepted general mechanism for the OH-initiated oxidation of aldehydes is shown in Figure 1.

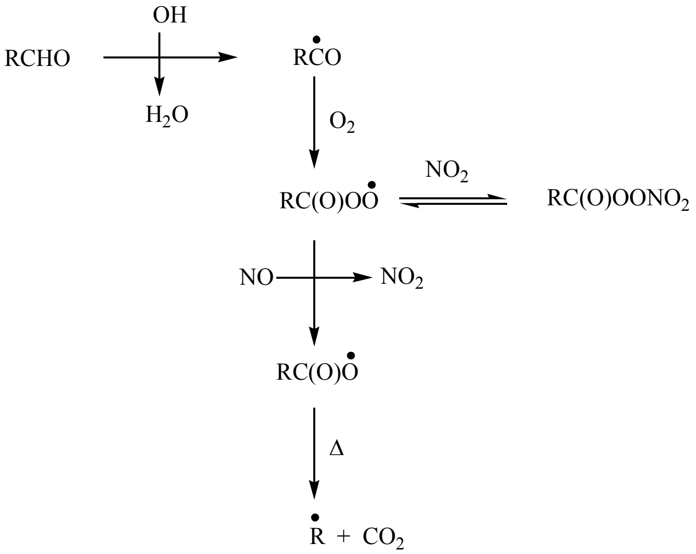

Figure 1. General Mechanism for the OH-initiated oxidation of aldehydes in the presence of NO_x (adapted from Atkinson and Arey, [2003]).

However, there is recent experimental evidence which suggests that alternative pathways may be available to the intermediate acyl (RCO) and acyl oxy (RC(O)O) radicals.

Prompt decomposition of acyl radicals

Acyl radicals can undergo two different processes, either reaction with oxygen:

$$RCO + O_2 + M \rightarrow RC(O)O_2 + M \quad (1)$$

or thermal decomposition:

$$RCO + M \rightarrow R + CO + M \quad (2)$$

The competition between these two processes is governed by the stability of RCO, which is known to vary considerably with the nature of R. If the chemical mechanism for the degradation of a particular aldehyde is not known, it is common practice to assume that the sole fate of the RCO radical is reaction with oxygen. Although this appears to be true when R is an alkyl group, theoretical and experimental results indicate that decomposition is also important when R contains a halogen or oxygen atom [Méreau *et al*., 2001]. Further evidence for the importance of the decomposition pathway was obtained in a recent study of the reactions of C_3F_7CO radicals [Solignac *et al.*, 2006], where a molar yield of over 60 % was obtained for CO. Preliminary results from the OH-initiated oxidation of *m*-tolualdehyde [Clifford *et al.*], where a CO yield of 13 % was obtained, indicate that the decomposition pathway may also be occurring for aromatic acyl radicals. However, the yield of the peroxyacyl nitrate was estimated to be 60 %, indicating that reaction with oxygen is still the major pathway in this instance.

In cases where decomposition of the acyl radical is occurring, the yield of the peroxyacyl radical and, in turn, the peroxyacyl nitrate, is obviously less than expected. This may have implications for the NO_x budget in the atmosphere. Clearly, further work is required to elucidate the importance of the decomposition pathway for other RCO radials.

Isomerization of acyl oxy radicals

Isomerization is an important reaction pathway for alkyl oxy (RO) radicals where $R \geq C_4$. This process occurs via a 1,5 H atom shift [Atkinson and Arey, 2003] and is often more favourable than the competing pathways, reaction with oxygen and unimolecular decomposition. It is possible that acyl oxy (RC(O)O) radicals could also undergo isomerization. However, there have been very few studies of the atmospheric oxidation of medium or long chain aldehydes and this reaction pathway has thus received virtually no attention. There are only two reported references to isomerization of acyl oxy radicals in the literature. Jenkin *et al.* [2000] proposed that formation of *cis*-pinic acid from the ozonolysis of α- and β-pinene occurs through isomerization of a C_9 acyl oxy radial via a 1,7 H atom shift and, more recently, Wang *et al.* [2006], suggest that an aromatic acyl oxy radical produced during the degradation of phthaldialdehyde, could undergo cylcization. In both cases, these isomerization reactions are in direct competition with the thermal decomposition pathway, which produces $R + CO_2$. It is generally assumed that this latter reaction is the dominant fate of all acyl oxy radicals. However, isomerization may be important for aldehydes with $R \geq C_4$. A possible reaction scheme showing isomerization of the acyl oxy radical produced during the atmospheric degradation of n-pentanal is shown in Figure 2. The molecular product of this pathway is a keto acid, which is likely to be incorporated into the condensed phase if formed in the atmosphere. Experimental studies of the atmospheric degradation of n-pentanal are currently underway in our laboratory in order to check the viability of this reaction pathway. If isomerization is found to be important for acyl oxy radicals then theoretical calculations will also be employed to investigate the energetics of the competing processes.

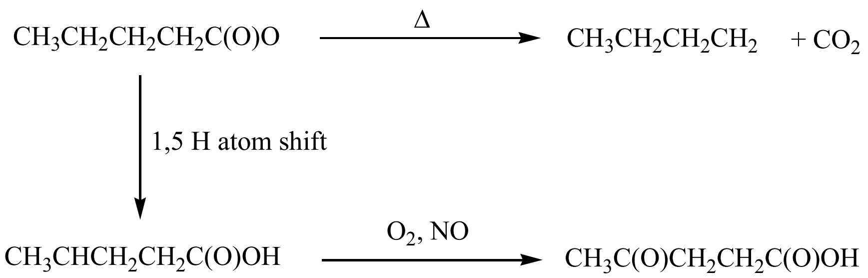

Figure 2. Possible reaction pathways for the acyl oxy radical produced during the OH-initiated oxidation of *n*-pentanal.

Future outlook

Recent experimental evidence suggests that alternative pathways are available to the intermediate acyl (RCO) and acyl oxy (RC(O)O) radicals produced during the atmospheric oxidation of alehdyes. Further experimental and theoretical studies are needed to understand the fate of RCO and RC(O)O radicals when R is not a simple alkyl group. The importance of these alternative pathways should be assessed and included in chemical models if necessary.

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Modelling the Global Impacts of VOC Oxidation

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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The oxidation of volatile organic compounds in the presence of nitrogen oxides (NO_x) is an important source of ozone in the troposphere on a global scale [Houweling *et al.*, 1998]. However, quantifying the magnitude of this source requires a good understanding of the VOCs present in the troposphere, their sources, chemical reaction mechanisms and kinetic rates, and their removal pathways. Current models of global tropospheric chemistry are computationally expensive and consequently include rather simplified treatments of hydrocarbon oxidation, and the uncertainty in their conclusions is large. Recent international global chemistry-transport model (CTM) intercomparison exercises have revealed large differences between models in their chemical budgets for ozone and methane [Stevenson *et al.*, 2006], despite relatively tight constraints in precursor emissions and meteorology, and treatment of hydrocarbon chemistry makes a major contribution to these differences.

FRSGC/UCI CTM studies of O_3 budget sensitivity

To calculate the global budget sensitivity of ozone and methane to hydrocarbon oxidation, the Frontier Research System for Global Change/University of California Irvine (FRSGC/UCI) CTM [Wild *et al.*, 2003] has been run at T21L19 resolution (5.6° × 5.6°) under a variety of different conditions. Increases in gross O_3 production with higher hydrocarbon emissions are shown in Figure 1 under different assumptions of global NO_x emissions. These results suggest that at current emission levels oxidation of non-methane hydrocarbons leads to formation of 1500 Tg/yr of O_3, about 30 % of total O_3 production, and about two-thirds of this is due to oxidation of isoprene. Hydrocarbons also contribute about 800 Tg/yr of CO, similar to the amount generated by CH_4 oxidation and about 25-30 % of the global CO source. Oxidation of non-methane hydrocarbons leads to an increase in CH_4 lifetime of almost 1 year, as faster removal of hydroxyl radicals (OH) outweighs additional production of OH from higher levels of O_3. Hydrocarbon oxidation thus contributes to radiative forcing of climate through increases in both O_3 and CH_4, as well as through the generation of secondary organic aerosol which is not considered here.

Uncertainty in global model studies

Recent model intercomparison exercises conducted within ACCENT have demonstrated that considerable uncertainty remains in the ability of the current generation of global chemical models to represent the tropospheric budgets of O_3, CO, CH_4 and VOC [Dentener *et al.*, 2006]. Global mean O_3 production over 21 models was found to be 5100 ± 600 Tg/yr (± 1σ), and the CH_4 lifetime was 8.7 ± 1.3 years [Stevenson *et al.*, 2006]. The production of CO from CH_4 oxidation was found to be 770 ± 140 Tg/yr, with yields ranging between 0.77 and 0.93, reflecting differences in oxidation pathways and in removal of soluble species [Shindell *et al.*, 2006]. Variations in CO production from non-methane hydrocarbon oxidation were significantly larger (730 ± 220 Tg/yr), indicating even larger uncertainties in VOC oxidation schemes. A central conclusion of the intercomparison is thus that model treatments of hydrocarbon oxidation are a major contributor to the differences seen between current global chemical models. An earlier comparison of commonly-used isoprene oxidation schemes suggested an uncertainty in the effects on global O_3 of the order of ± 35 % [von Kuhlmann *et al.*, 2004]. In addition to uncertainty in VOC emission rates (minimized in the ACCENT intercomparison by use of supplied emission fields) the largest uncertainties are in the representation of chemical schemes, in the balance of OH, O_3 and NO_x in the model defining which reaction pathways are followed, and in removal and scavenging of soluble intermediates. Further development of these models to include more detailed treatment of secondary organic aerosol formation, currently missing from most of them, is likely to lead to greater differences between them.

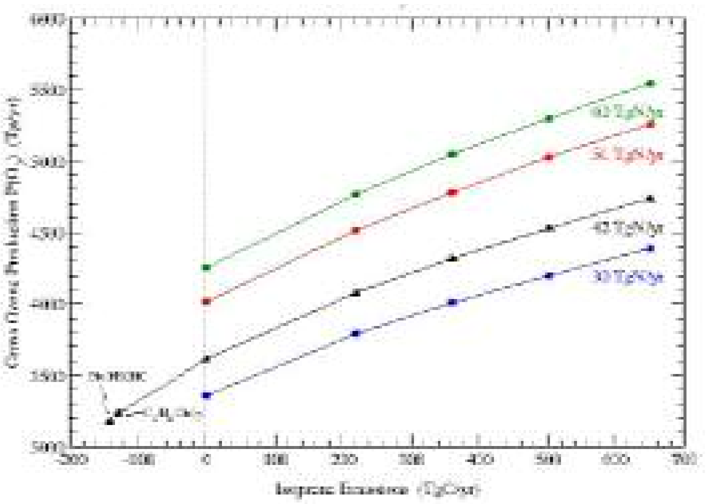

Figure 1. Sensitivity of global tropospheric ozone production to emissions of isoprene (C_5H_8) for different global NO_x emissions. Current conditions are represented by isoprene emissions of 500 TgC/yr and NO_x emissions of 51 TgN/yr.

Modelling challenges

The next generation of global-scale Earth System models including tropospheric chemistry will continue to require highly simplified representations of VOC oxidation so that feedbacks between climate, biogenic emissions, tropospheric chemistry, aerosols and clouds can be represented. These schemes will need to capture the key impacts important for ozone and aerosol formation on appropriate scales: the magnitude and timescales for peroxy radical formation, temporary storage and removal of C and N via organic nitrate transport and deposition, and formation of secondary organic aerosol. Mechanism reduction for these purposes requires optimization over both reactivity and condensability, and will need to be based on a deeper understanding of hydrocarbon oxidation and scavenging processes than was available during development of current CTM chemistry schemes.

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Global Observations of Formaldehyde and Glyoxal from Space

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Summary

The Institute of Environmental Physics of the University of Bremen hosts an interdisciplinary research group focusing on the investigation of the atmosphere, the cryosphere, and the oceans of the earth. Part of the IUP is the DOAS group which works on UV/visible remote measurements of atmospheric composition using the Differential Optical Absorption Spectroscopy-Method (DOAS). Although the DOAS technique was developed to analyse ground-based zenith-sky and active long-path measurements, it can also be applied to satellite borne measurements in the UV and visible, if they provide enough spectral resolution to make use of the differential part of the absorptions. This work describes global measurements of the trace gases formaldehyde and glyoxal derived from stray light spectra measured by the satellite instruments GOME and SCIAMACHY [Wittrock, 2006; Wittrock *et al.*, 2006].

Introduction

The objectives of this work are to investigate the global distribution of oxygenated volatile organic compounds (OVOC) in order to improve our knowledge on the emissions and the chemical fate of VOCs in the atmosphere. Methane (CH_4) and non-methane hydrocarbons (NMHC) are released into the atmosphere by a variety of natural and anthropogenic sources. The CH_4 oxidation ultimately produces HCHO, carbon monoxide (CO) and finally carbon dioxide (CO_2). NMHC react with hydroxyl (OH) radicals and other oxidizing agents, forming aldehydes, ketones and organic acids. In the presence of nitrogen oxides (NO_x), CH_4 and NMHC foster the photochemical production of ozone (O_3). HCHO is formed in most NMHC oxidation chains and also has known primary emissions from fossil fuel and biomass burning as well as industrial activities. They are, however, negligible compared to its large secondary source from volatile organic compounds (VOC) oxidation with the main single compound precursors methane and isoprene. HCHO is used as a proxy for VOC emissions. In spite of much progress in the last decade, emission estimates for the majority of NMHC remain quite uncertain (*e.g.* [Wiedinmyer *et al.*, 2004]).

Measurements of tropospheric HCHO have been made over the past three decades mainly on a campaign basis by both remote sensing and in situ techniques in urban and remote locations (*e.g.* [Hak *et al.*, 2005] and references therein). With the launch of GOME (Global Ozone Monitoring Experiment) instrument in April 1995 formaldehyde measurements from space became feasible for the first time ([Burrows *et al.*, 1999] and references therein). Regions with elevated HCHO concentrations have been identified using GOME observations and linked to biogenic isoprene emissions, biomass burning and also urban pollution [Chance *et al.*, 2000; Thomas *et al.*, 1998].

Glyoxal, CHOCHO, the simplest alpha dicarbonyl organic compound, is formed from the oxidation of a variety of hydrocarbons [Volkamer *et al.*, 2001; Volkamer *et al.*, 2005c]. Tropospheric CHOCHO has been measured during several campaigns. For example, in the boundary layer of a rural site, Lee *et al.* [1998] and Munger *et al.* [1995] have reported mean mixing ratios of 0.07 ppb_V and 0.04 ppb_V glyoxal, respectively. The sources were thought to originate from isoprene rather than from anthropogenic emissions. Spaulding *et al.* [2003] found lower values of about 0.03 ppb_V above a ponderosa pine plantation in California. [Ho and Yu, 2002] have identified CHOCHO and other aldehydes in air masses affected by biomass burning, domestic and residential log fires. In Volkamer *et al.* [2005a] glyoxal has been found in Mexico City as a secondary photochemical product in traffic related emissions with values up to 1.8 ppb_V, while direct CHOCHO emissions from traffic were small (< 4 %). This study also reported the first direct spectroscopic observations of CHOCHO in the atmosphere. During the day, photolysis and reaction with OH determine the CHOCHO lifetime. This was found to be 1.3 hours for overhead sun conditions, as compared to about 1.6 hours for HCHO [Volkamer *et al.,* 2005a]. Global observations of CHOCHO from space offer the potential of identifying photochemical hot spots in the earth's atmosphere [Volkamer *et al.,* 2005a], and coupled with observations of HCHO constrain our understanding of biogenic emissions, biomass burning, and urban pollution.

Scientific activities

For the retrieval of vertical columns of HCHO and CHOCHO from the satellite observations, the well established DOAS technique has been used. Briefly, the DOAS approach relies on the separation of narrow band absorption signatures from broad band absorption and scattering features. Retrievals comprise the determination of the slant column absorption for the gas and its conversion to a vertical column amount by an air mass factor, AMF. This accounts for the path of light through the atmosphere and takes the vertical profiles of scattering and absorbing species into account [Wittrock *et al.*, 2004].

For the HCHO column amounts, the DOAS spectral window, the non-linear least-squares fitting procedure, and reference spectra have been developed for GOME [Wittrock *et al.*, 2000]. For the fitting of SCIAMACHY data, a spectral region of 334 – 348 nm was selected to avoid any correlation with an instrument grating polarisation structure around 360 nm. The AMF calculations use a priori knowledge of vertical HCHO profiles (see Wittrock [2006] for details).

For the determination of the CHOCHO column amounts, the spectral region 436 – 457 nm was selected as optimal for fitting. In this case, the absorption cross sections of CHOCHO [Volkamer *et al.*, 2005b] O_3, NO_2, H_2O, O_4, a Ring spectrum, which accounts for both rotational and vibrational Raman scattering, and a quadratic polynomial are included in the fitting procedure.

Scientific results and highlights

In Figures 1 and 2, the global composites of HCHO (GOME) and CHOCHO (SCIAMACHY) are depicted. Enhanced column amounts of $\geq 1 \times 10^{15}$ molec·cm^{-2} for CHOCHO and $\geq 1.5 \times 10^{16}$ molec·cm^{-2} for HCHO are mainly observed in South America, Africa and Asia. In South America, high column values can be found in the Amazon Basin, the world's largest tropical rain forest, and low values are found over the Andes. In Africa, elevated levels are found over the tropical rain forests and in regions having regular biomass burning events, for example, in Ghana. In Asia, large values of both trace gases are observed over Cambodia, Thailand, Sumatra, Borneo, south of the Himalayas in India and Nepal and above densely populated areas in China. Generally, the pattern observed for CHOCHO is similar to the global picture of HCHO, indicating common main sources.

CHOCHO column amounts retrieved over water are influenced by interference from liquid water absorption. This can lead to negative values above clear water regions. Inclusion of a liquid water reference spectrum in the fitting procedure for water ground scenes reduces these artefacts. Nevertheless, measurements over water have to be interpreted with care. Several regions above the oceans display significantly elevated CHOCHO amounts, including biologically active regions: for example, near the equator, over the Indian Ocean and close to the coast of China.

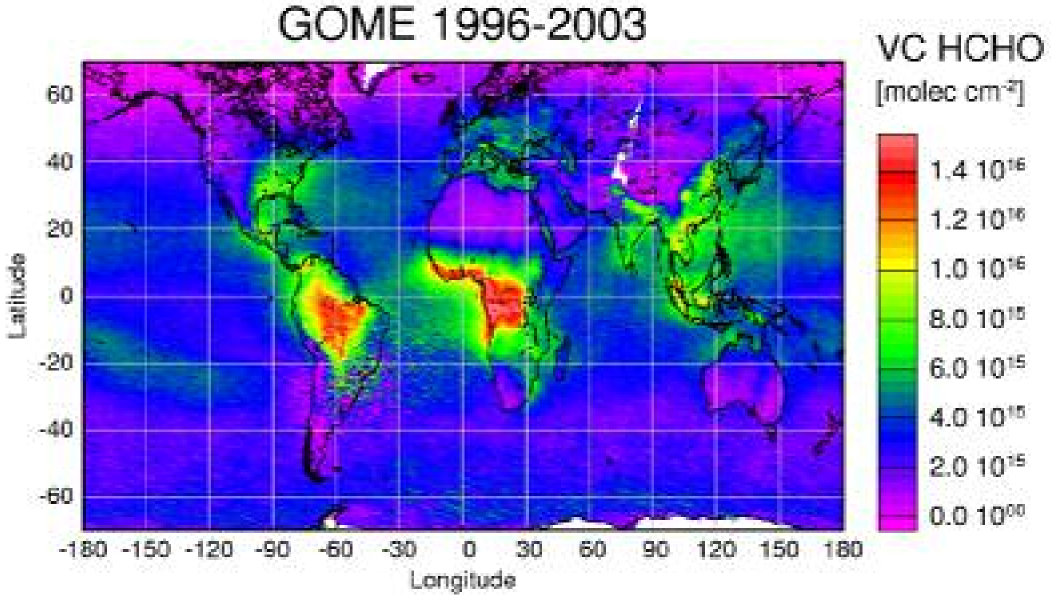

Figure 2. Yearly mean of HCHO derived from GOME observations from April 1996 to March 2003. Desert areas as well as mountain sites exhibit the lowest amounts of HCHO, highest amounts show up above tropical rain forests.

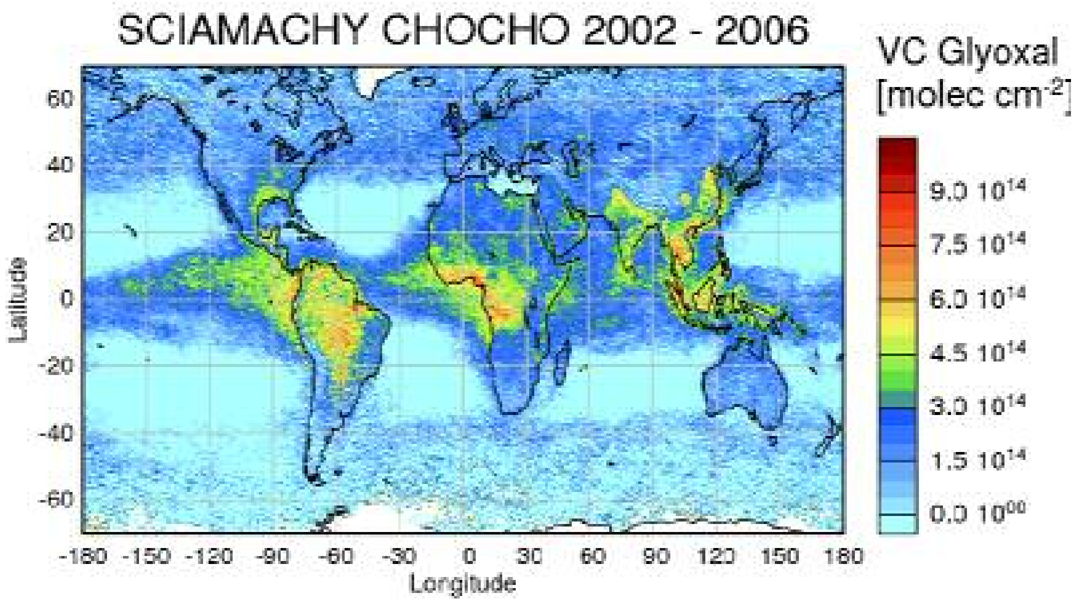

Figure 3. Multiannual mean for CHOCHO derived from SCIAMACHY observations from August 2002 to July 2006. The pattern is quite similar to that of formaldehyde which supports prospects on similarities of precursors for both trace gases.

As is the case for HCHO, the Pacific region between the Galapagos Islands and the coast of Colombia exhibit large amounts of CHOCHO of up to 8×10^{14} molec·cm^{-2}. This is potentially due to the outflow of terrestrial sources of the VOC precursors of HCHO and CHOCHO and the possible presence of biogenic VOC sources over the biogenically active oceanic regions. In this context, Warneck [2005] has pointed out in a box model study that glyoxal is a prominent oxidation product from, for example, acetylene and ethene in the marine troposphere. However, another spectral interference of the CHOCHO analysis with chlorophyll absorption can not be excluded and might lead to an overestimation of glyoxal amounts.

In the global composite maps of HCHO and CHOCHO, the regions with large biogenic emissions have the largest local column amounts. However, for selected areas and time periods, biomass burning also produces significant amounts of both, glyoxal and formaldehyde (Figure 3).

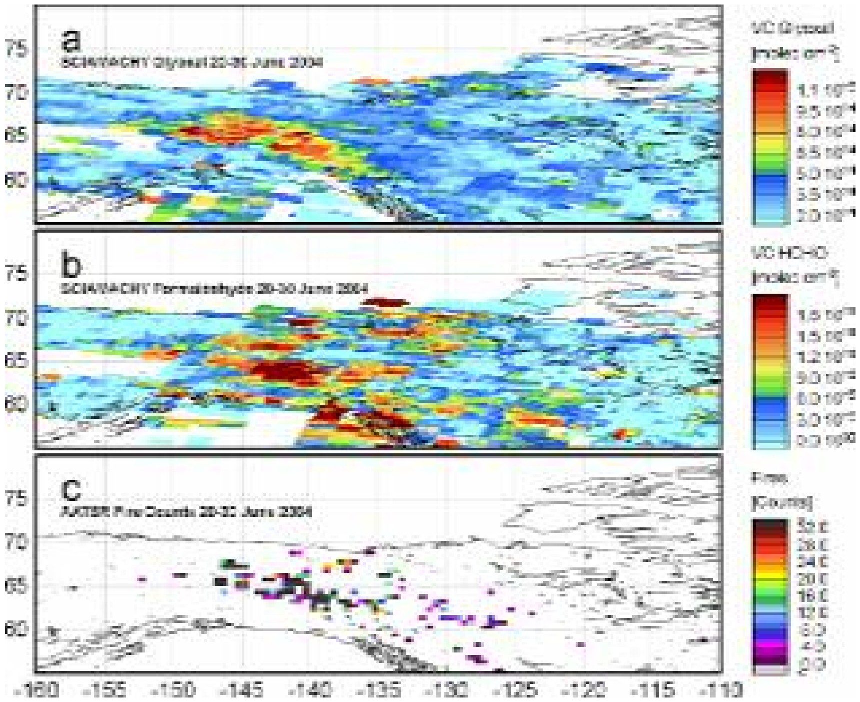

Figure 4. Observation of formaldehyde and glyoxal during massive biomass burning in Alaska in June 2004.

Future outlook

An extensive validation of the satellite measurements with ground-based data is necessary and possible (see, for example, www.doas-bremen.de for information on the BREDOM network of MAX-DOAS instruments). In order to confirm (or falsify) the presence of significant amounts of HCHO and CHOCHO over the oceans, dedicated MAX-DOAS measurements from ships will be taken during latitudinal transects. Detailed comparisons between measurements and model results, coupled with retrievals of other trace gases such as NO_2, will constrain our knowledge of VOC chemistry in the current generation of atmospheric models.

Data from new satellite instruments providing better spatial resolution and more coverage such as OMI and GOME-2, but even more so the proposed geostationary instruments should be able to provide much more detail on the spatial and temporal variation of both formaldehyde and glyoxal and their sources, and at the same time make validation with local measurements more practical and thereby improve absolute accuracy over what could be achieved within this work.

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Comparison of Global Observations of Formaldehyde with Model Results

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 2

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Summary

Here, a systematic comparison of HCHO columns obtained from the GOME instrument (see workshop contribution on “Global observations of formaldehyde and glyoxal from space” for more general information on the measurements) with a state-of-the-art model is presented. This comparison comprises the years 1997 to 2001 and is the first study, where long-term global observations of HCHO are compared to model output. This work has been carried out within the European project RETRO.

Introduction

The main objectives of this work are to identify the key uncertainties in the current representation of volatile organic compound (VOC) emissions and VOC chemistry in global models. VOCs play an important role in oxidiation chemistry in the troposphere ([Poisson *et al.*, 2000] and references therein).

Scientific activities

For the retrieval of vertical columns of HCHO from GOME, the DOAS technique has been used. Briefly, the DOAS approach relies on the separation of narrow band absorption signatures from broad band absorption and scattering features. Retrievals comprise the determination of the slant column absorption for the gas and its conversion to a vertical column amount by an air mass factor, AMF. This accounts for the path of light through the atmosphere and takes the vertical profiles of scattering and absorbing species into account [Wittrock *et al.*, 2004]. Here, vertical column densities have been calculated using the AMF look-up tables (see Wittrock [2006] for details). To account for the degradation of the GOME instrument which results in offsets of the retrieved HCHO slant columns, monthly averages have been normalised to a reference region in the Pacific. For this, it is assumed that the formaldehyde column in that region has only small seasonal and year-to-year variation. All GOME data presented here were gridded on the spatial resolution of the model (3.75° × 2.5°). Further adaptations were not applied (*e.g.* using model data for a reference sector).

The LMDz (Laboratoire de Meteorologie Dynamique, zoom) is a grid point General Circulation Model (GCM) developed initially for climate studies by Sadourny and Laval [1984]. In LMDz the finite volume transport scheme of Leer [1977] is used to calculate large-scale advection of tracers. The parameterisation of deep convection is based on the scheme of Tiedke [1989] and a local second-order closure formalism is used to describe turbulent mixing in the planetary boundary layer (PBL). The Interactive Chemistry and Aerosols (INCA) model has been integrated into LMDz. INCA simulates tropospheric chemistry, emissions and deposition of primary tropospheric trace species including non-methane hydrocarbons. The INCA chemical scheme includes 85 chemical species and 303 chemical reactions. A detailed description and evaluation of LMDz-INCA can be found in Hauglustaine *et al.* [2004], Folberth *et al.* [2005] and Lathiere *et al.* [2005].

This five-year simulation was performed, using the nudged version for meteorology (*i.e.* meteorological fields are relaxed toward the ERA40 reanalysis). Regarding emissions, anthropogenic emissions are from the EDGAR V2.0 inventory [Olivier, *et al.*, 1994], biomass burning emissions are those of [van der Werf, *et al.,* 2003; van der Werf, *et al.,* 2004], biogenic emissions are from GEIA [Guenther, *et al.,* 1995] and aircraft emissions are provided by the NASA. Two different runs were carried out: one with a static scenario for biomass burning (run 33), the other one considering the inter-annual variability of biomass burning (run 34). The model output is analysed at 10:30 local time, close to the overpass time of the satellite.

Scientific results and highlights

Figure 1 shows the mean formaldehyde columns from GOME. The corresponding model results for the same time period from 1997 to 2001 are illustrated in Figure 2. The pattern of the main source regions of formaldehyde in the tropics as well as the general latitudinal distribution and the seasonal trend with higher values in each hemisphere in summer (not illustrated here) are in good agreement. While the correlation coefficient for measurement and model is high (overall 0.81) and also for land and ocean separately (0.89 and 0.83, respectively), the model systematically overestimates the formaldehyde over land in particular above South America and underestimates HCHO over most parts of the oceans.

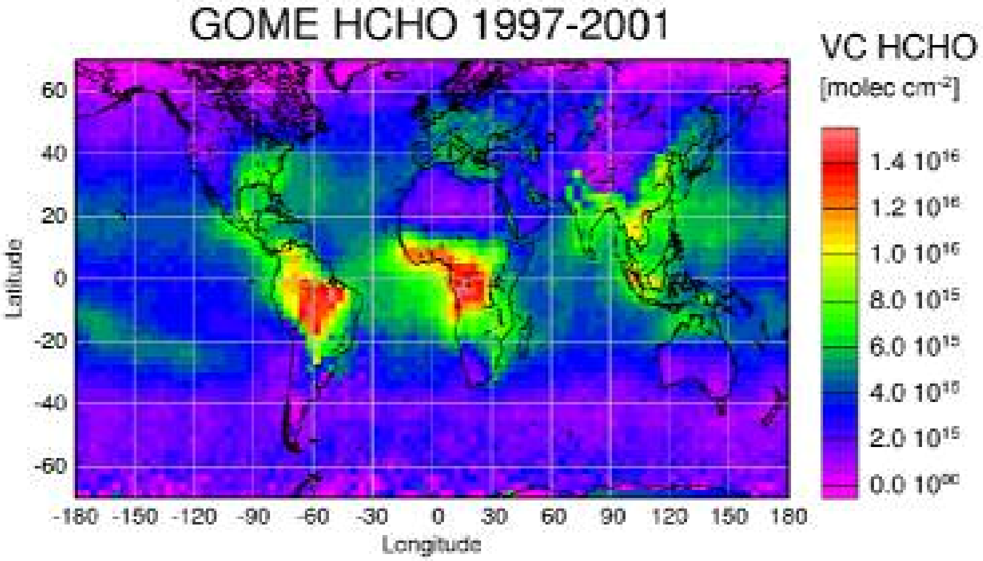

Figure 1. Mean values from GOME on model resolution (2.5° × 3.75°) derived from monthly means from January 1997 to December 2001.

The transport of isoprene and formaldehyde seems to be an unlikely explanation of the high columns observed over some oceanic regions due to their short lifetime of up to a few hours only. Transport over distances of about 50 to 150 km is feasible, but not long-range transport as would be necessary to explain the high values *e.g.* west of Africa. Two other explanations are possible: *in situ* production of HCHO from other more long-lived precursors or an oceanic source.

In particular, biomass burning plumes are known to contain high concentrations of other hydrocarbons [Holzinger *et al.*, 2005; Price *et al.*, 2004], and little is known on the atmospheric chemistry and fate of these substances, which are not included in the INCA model run. Similarly, biogenic emissions from forests are not limited to isoprenes and monoterpenes, and potentially other molecules which are correlated to isoprene emissions could act as HCHO precursors. In addition, recycling mechanisms within an aging plume are conceivable, but at this point mere speculation.

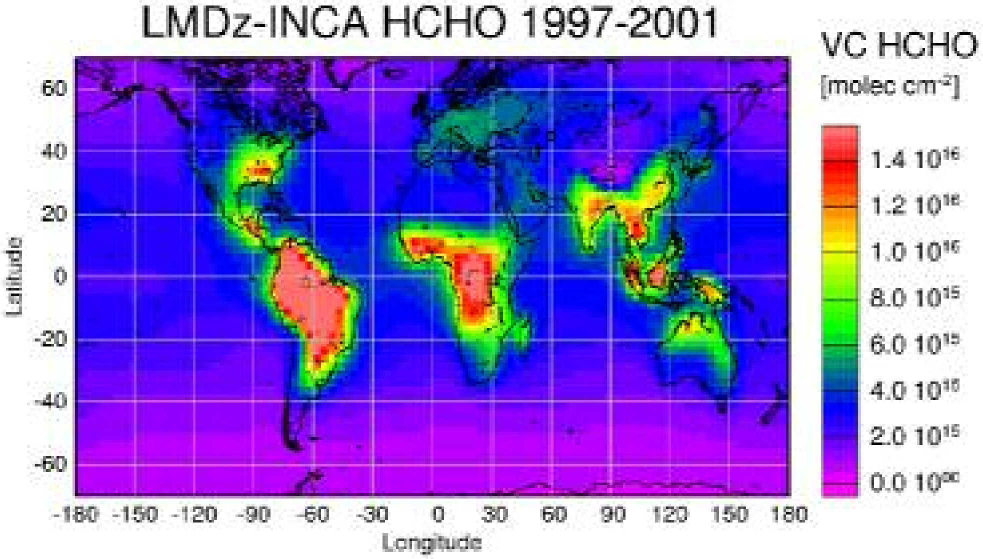

Figure 2. Mean values from model – here, the run taking into account the annual variability of biomass burning was utilised (run 34).

For selected regions, the seasonal cycle of GOME formaldehyde is compared to model data over a time period of five years. The regions were selected in order to obtain a representative set with different scenarios like biogenic emissions, biomass burning and anthropogenic emissions. Here, a subset of these regions is shown.

The oak forests in the so-called Ozarks of south eastern North America are efficient emitters of isoprene [Wiedinmyer *et al.*, 2001; Wiedinmyer *et al.*, 2005]. Depending on light intensity as well as growing season (May to August) formaldehyde production is expected to be largest in summer, which is reflected by measurement and model (see Figure 3, upper panel). The seasonal cycle correlates by 0.95 indicating a good representation of the biogenic sources and their seasonality in the model. This is not surprising as these areas are amongst the most intensely studied and best characterised, and have in fact already been compared to measurements in previous studies [Abbot *et al.,* 2003; Chance *et al.*, 2000; Palmer *et al.*, 2003]. However, the wintertime background levels of 0.5×10^{16} molec/cm^2 are not confirmed by the measurements indicating a too large source of isoprenes in winter. On the other hand, as these values are rather low, measurement errors cannot be neglected and the lack of a signal could at least in parts be related to the detection limit of the GOME data.

In Brazil (see Figure 3, lower panel) the amplitude and also the time of maximum formaldehyde of the seasonal variation is reproduced nicely by the model. The correlation for the model run 34 to the measurement is 0.91. Maximum formaldehyde correlates with the burning season in this region in summer. However, over the time period of five years the average model column is almost a factor of two larger. The year-round background values of about 0.8×10^{16} molec/cm^2 are caused by biogenic emissions which seem to be significantly overestimated in the model. For the measurements, cloud contamination over the rain forest could be a reason for a systematic underestimation, but a study on the dependence of HCHO columns on cloud fraction does not give any indication for such an effect. This point will have to be revisited once satellite measurements with higher spatial resolution and thus less cloud problems become available, *e.g.* OMI.

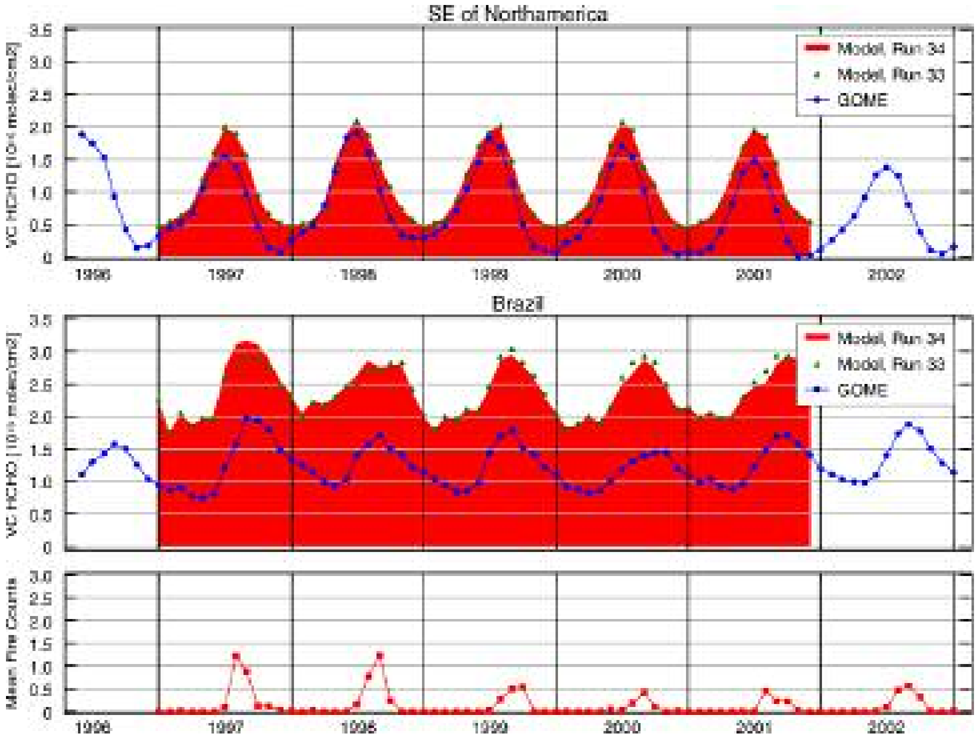

Figure 3. Comparison between GOME observations and model for regions in America.

Figure 4 illustrates the situation in Africa: Due to the ITCZ, the dry season and consequently the burning season are shifted in time in the two selected regions of Ghana and Congo. The measurements of formaldehyde display a seasonal cycle with a maximum at the time of biomass burning. Although the amplitude of model and measurement of this seasonal cycle as well as the average column agree well, the phase of the measurements is completely missed and rather exhibits a double maximum indicating model deficiencies in the parameterisation of the emission of biogenic precursors and their timing. Again, contamination by clouds and biomass burning aerosols could be a problem for the satellite measurements, but the overall consistency of the measurements is more indicative of a model deficiency.

In addition to the continental regions, also an area over the Atlantic close to Africa was selected: Here, the model only shows the background formaldehyde produced by methane oxidation whereas GOME sees on average a 60 percent higher column (see Figure 4, lower panel) readdressing the discussion about *in situ* formation of formaldehyde. It is notable, that the small seasonal variation above the ocean does not correlate with biomass burning above the Congo region. This might be a hint that rather biogenic emissions than plumes of biomass burning cause the elevated levels of HCHO above water.

Future outlook

The comparison of modelled and measured HCHO fields should be extended by systematic variation of emission parameters and their implementation in the model to identify the key uncertainties. Also, glyoxal data (see other contribution of Wittrock *et* *al.* to this workshop) should be included in the comparison. Another logical step is the comparison of satellite and in particular ground-based MAX-DOAS measurements with regional models.

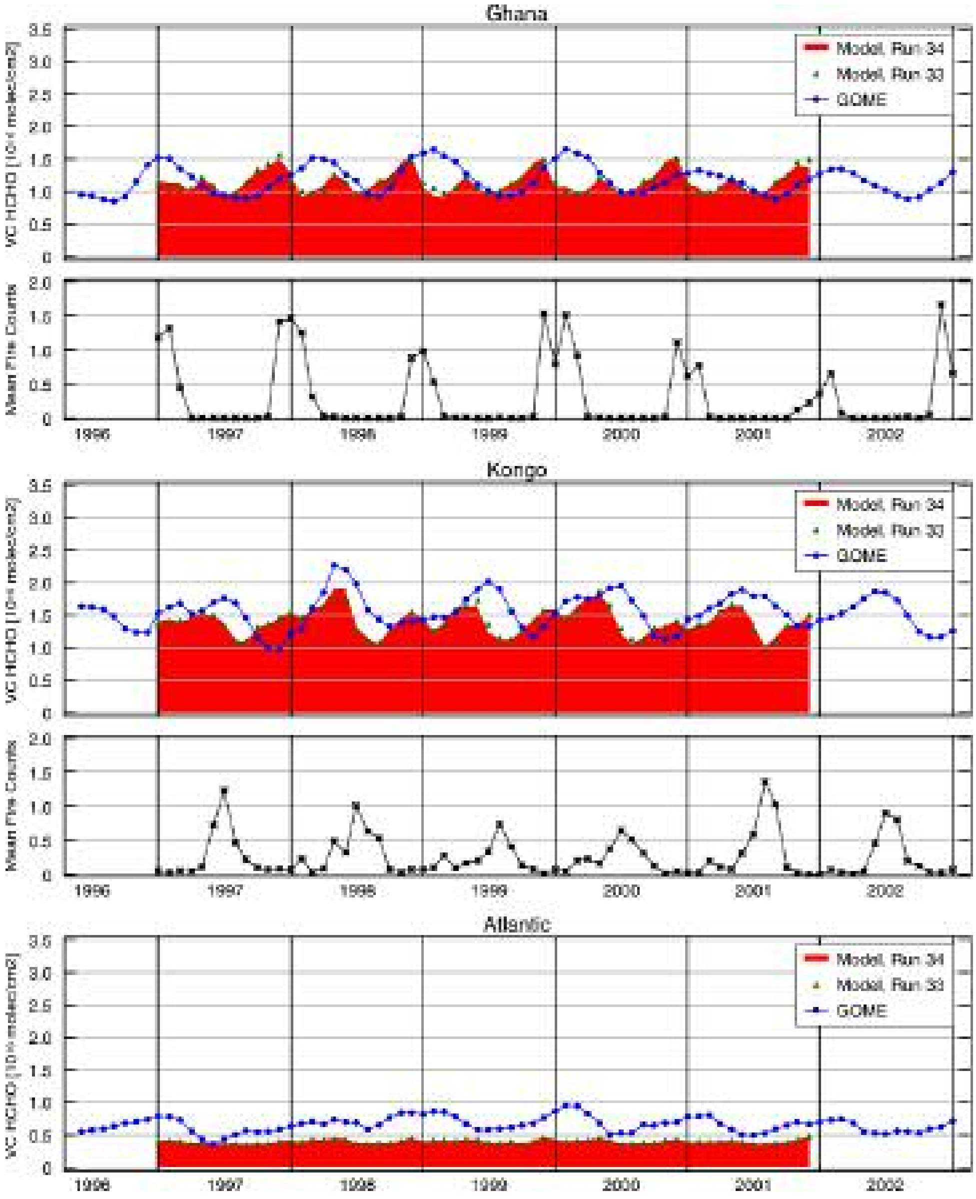

Figure 4. Comparison between GOME observations and model for regions in Africa.

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

11. Contributions from the Participants in Group 3

Differences in SOA in the North and the South of the Alps: A Modelling Study

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Summary

The formation and transport of secondary aerosols during a short period in summer 2003 were studied with MM5/CAMx model system over an area covering Switzerland and surrounding countries. The modeled components were secondary inorganic and organic aerosols (SOA), with a particle diameter smaller than 2.5 µm. Differences between the regions in the north and the south of the Alps were investigated with respect to the aerosol concentrations and contribution from anthropogenic and biogenic sources. The importance of the enthalpy of vaporization (ΔH_{vap}) values used in the model for the temperature dependence of SOA were also discussed. The contribution of biogenic sources to SOA was predicted to be rather high, about 70 % in the north, whereas it was lower in southern Switzerland (40 %) and in northern Italy (15-25 %). These results agree well with measurements. The sensitivity tests with modified ΔH_{vap} values suggest that 20 % variations do not affect SOA calculations significantly at air temperatures below 20 °C in the whole model domain. At higher temperatures, SOA levels can be substantially influenced.

Introduction

PM concentrations in Switzerland frequently exceed the threshold values. The long-term measurements of atmospheric PM and their chemical composition indicate that organic matter, nitrate and sulfate are the main contributors to the annual $PM_{2.5}$ mass concentrations at rural, near-city and urban background sites in Switzerland [Gehrig and Buchmann, 2003, Hueglin *et al.*, 2005]. Understanding the partitioning behavior of semi-volatile species between the gas and aerosol phases can help us to predict how changes in anthropogenic and biogenic activity will influence the formation of aerosols in the atmosphere. With this understanding, appropriate control strategies can be developed.

Modelling secondary organic aerosol (SOA) formation is among the most demanding aspects associated with atmospheric organic photo oxidation because the formation process depends on a) the representation of the parent organic species that lead to condensable products after being oxidized, b) the gas-phase chemistry where condensable species are formed, and c) the representation of the gas/particle partitioning process of the condensable compounds. The temperature dependence of SOA formation is another key point of uncertainties affecting models. Some studies suggest that current models underestimate SOA concentrations [Zhang *et al.*, 2004, Cousin *et al.*, 2005]. Recent experimental evidence for oligomerization reactions in organic aerosols indicated the need to readdress the current assumptions in models about the partitioning of oxidation products in the gas and the particle phase [Kalberer *et al.,* 2004]. Recent evidences suggest that sesquiterpenes and isoprene can also form SOA compounds that are not yet accounted for in most of the models [Morris *et al.*, 2006]. In Switzerland, there is hardly any model study on aerosols yet [Andreani-Aksoyoglu *et al.*, 2003]. In view of the forthcoming European legislation on particles, air quality simulations including aerosol processes are urgently needed. This study on modeling of secondary aerosols provides information about their formation and the contributions from anthropogenic and biogenic activities around the Alpine regions.

Methods

In this study, the 3-dimensional photochemical model CAMx (Comprehensive Air Quality Model with Extensions, version 4.11s) was used with CBMIV chemical mechanism [Environ, 2004]. The two nested domains cover the central part of Europe (resolution of 27 km × 27 km) and Switzerland with surrounding countries (resolution of 9 km × 9 km), respectively. There are 10 σ-layers in a terrain-following coordinate system, the first being about 40 m above ground. The coordinate system used in this study is the Lambert Conic Conformal system. The model top corresponds to about 550 hPa. Simulations started on 4th August 2003 at 0000 UTC and ended on 7th August at 2400 UTC. Meteorological data were generated by the MM5 meteorological model [PSU/NCAR, 2004]. MM5 was initialized by data of the Alpine Model (aLMo) of MeteoSwiss. During the studied period, southern Switzerland was under the influence of southerly winds bringing polluted air from the Po Basin. The emission inventory was prepared by compiling European and Swiss anthropogenic emissions from various data sources. Using land use and meteorological data, biogenic emissions were calculated by means of temperature and irradiance dependent algorithms [Andreani-Aksoyoglu and Keller, 1995]. Initial and boundary conditions were obtained from the regional European model REM-3/CALGRID. Calculations of aerosols with $d < 2.5$ μm were performed with the fine/coarse option of the aerosol module. The aerosol precursors are supplied to the aerosol chemistry module, which performs the following processes: aqueous sulfate and nitrate formation in cloud water using the RADM aqueous chemistry algorithm [Chang *et al.*, 1987], partitioning of condensable organic gases to secondary organic aerosols to form a condensed organic solution phase using a semi-volatile equilibrium scheme called SOAP [Strader *et al.*, 1998], partitioning of inorganic aerosol constituents (sulfate, nitrate, ammonium, sodium, and chloride) between the gas and particle phases using the ISORROPIA thermodynamic module [Nenes *et al.*, 1998].

Results and highlights

The model simulations suggest that the contribution of biogenic SOA to total SOA is rather high, about 70 % in the north (see Figure 1). ^{14}C measurements of different carbonaceous particle fractions from ambient aerosols showed that the water soluble organic compounds contained 65-82 % biogenic carbon at Zurich in summer [Szidat *et al.*, 2004, 2006].

The SOA concentrations of 2.3 μg/m^3 and the high biogenic fraction reported by Szidat *et al.* [2006] agree well with the model prediction of 2.7 μg/m^3 and 65 % biogenic contribution in Zurich. The large biogenic contribution in northern Switzerland is caused mainly by the Norway Spruce forests due to their abundance and high monoterpene emissions [Andreani-Aksoyoglu and Keller, 1995]. On the other hand, the biogenic contribution is substantially lower in southern Switzerland (about 40 %) and in the polluted area in northern Italy (25 %). The modeled biogenic contribution to SOA in northern Italy is in agreement with our previous predictions [Andreani-Aksoyoglu, *et al.*, 2004].

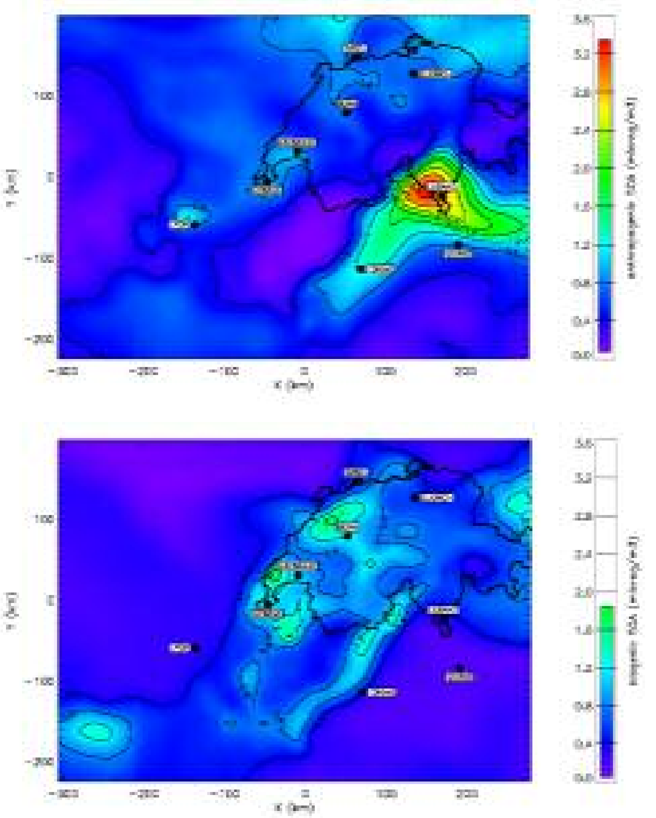

Figure 1. Modelled concentrations ($\mu g/m^3$) of anthropogenic (top) and biogenic (bottom) SOA ($d < 2.5$ µm) on 7th August 2003, 1500 UTC.

The formation of semi-volatile secondary organic compounds is based on the partitioning theory [Strader, 1999]. The temperature dependence of vapour pressures of species is described by the Clausius-Clapeyron equation in the models. The use of this equation requires the values of ΔH_{vap} to be known for each species. An average value of 156 kJ/mol for secondary organic aerosol species was given by [Strader, 1999]. We studied the sensitivity of the model to this value by varying it by 20 % in both directions. Changes in SOA concentrations in the afternoon due to a 20 % variation of ΔH_{vap} are shown in Figure 2. It should be noted that the saturation temperature in the model is given as 281.5 K and the afternoon temperatures in the model domain are all above the saturation temperature (see Figure 2, left). Increasing ΔH_{vap} leads to a decrease in SOA concentrations and vice versa. The correlation of this tendency with temperature indicates that SOA concentrations become sensitive to DHvap only at temperatures above 20°C.

Future outlook

At present, we are studying PM formation and transport with long-term simulations in winter as well as summer 2006. Measurements of aerosols in urban and motorway sites in northern Switzerland suggest that organics are the major components of the aerosol composition in winter, and they are mostly secondary. The modelling of SOA formation in winter for the first time in this region will provide valuable information about the importance of biogenic activity and the capability of the model system under winter conditions. A comparison of our results over the complex terrain with another aerosol model (CMAQ/MADRID) is also planned within a Swiss-Canadian collaboration.

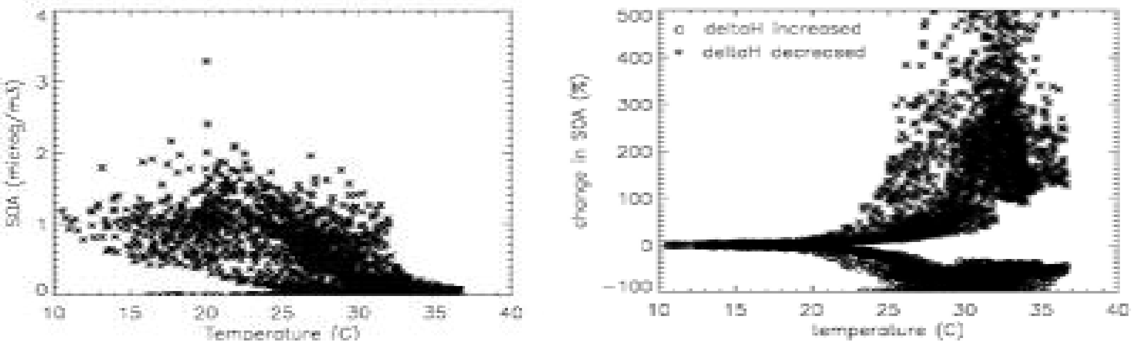

Figure 2. Left: Correlation of SOA concentration (μg/m^3) with air temperature in whole model domain using ΔH_{vap} =156 kJ/mol. Right: Change in SOA mass concentration (%) as a function of air temperature when ΔH_{vap} was decreased to 125 kJ/mol (asterisks) and increased to 187 kJ/mol (circles), respectively.

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How Important are SOA in Determining the Aerosol Size Distribution?

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Atmospheric aerosols are mixtures of inorganic and organic species. They are typically divided in aitken, accumulation and coarse modes which are lognormal size distributions with diameters approximately 0.01, 0.1 and 1 μm and standard deviations of approximately 2. Typical number concentrations of aerosols are 1000 to 100000 cm^{-3}. Examples of size distributions from particular areas and situations can deviate from this simple classification and are given by Jaenicke [1993], and Seinfeld and Pandis [1998]. It is important to understand why the atmospheric aerosol size distribution is the way it is. For example, Dusek *et al,* [2006] recently reported that the number of Cloud Condensation Nuclei (CCN) was mainly determined by the aerosol size distribution.

Secondary organic aerosols can potentially be crucial in forming the size and number concentration of atmospheric aerosols for at least two reasons: 1) When low volatile atmospheric species condense on the aerosols, they grow to larger sizes. Thereby they influence the modal diameters and standard deviation. 2) According Kulmala [2003] and Kulmala *et al,* [2004], condenseable organic vapours can explain growth of nucleation size (3 nm) molecules to aitken mode sizes. Kulmala *et al,* [2004] proposed a thermodynamic model for calculating saturation vapour pressures of organic vapours on nucleation mode aerosols.

Several models have been developed to calculate the influence of condenseable material on the aerosol phase. However, these models often use simplifications. Some models (*e.g.* Korhonen [2004]) fix gas phase concentrations, and thereby de-couple the gas phase chemistry from the aerosol dynamics. Other models calculate a bulk chemical equilibrium between the total aerosol phase and the total gas phase [Griffin *et al*, 2005]. Grini *et al,* [2005] fixed equilibrium saturation pressures of condensable organic vapours, and showed that interaction between photochemistry and aerosol dynamics could be important in determining the aerosol number concentration.

In the project “Aerosol/gas-phase chemistry and microphysics in global models”, funded by the Norwegian Research council, a sub-goal is to develop a detailed, sectional model to try to understand the properties of the aerosol size distributions. This project started in August 2006.

Model description

This works aims at allowing the gas phase concentrations to change freely, and calculate explicit fluxes by condensation and evaporation to and from different size sections. The principle of this sysstem is given in Figure 1. The figure shows an aerosol particle with concentration C_{aer} and a gas phase concentration C_{∞}The system will approach an equilibrium state through gas phase species condensing towards the aerosols. All size bins will have their particular surface equilibrium concentrations, C_S. The difference between the vapour concentration at the aerosol surface and the current bulk gas phase concentration decides the flux towards the aerosols.

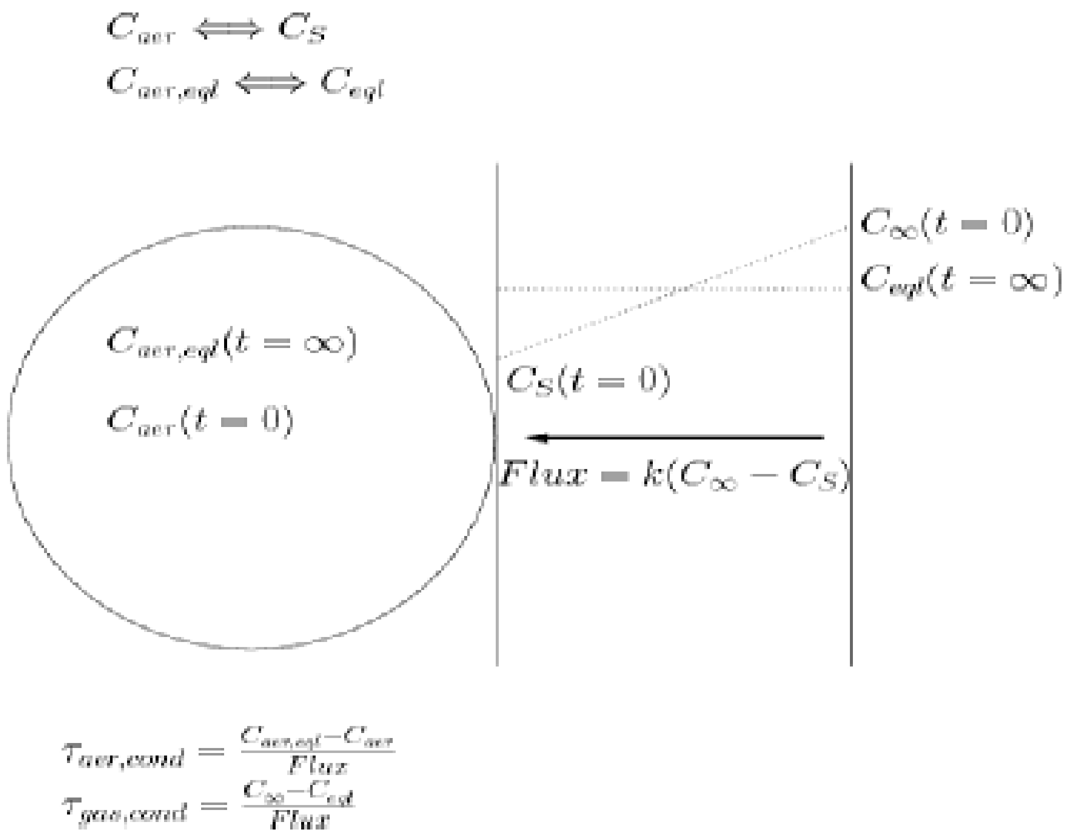
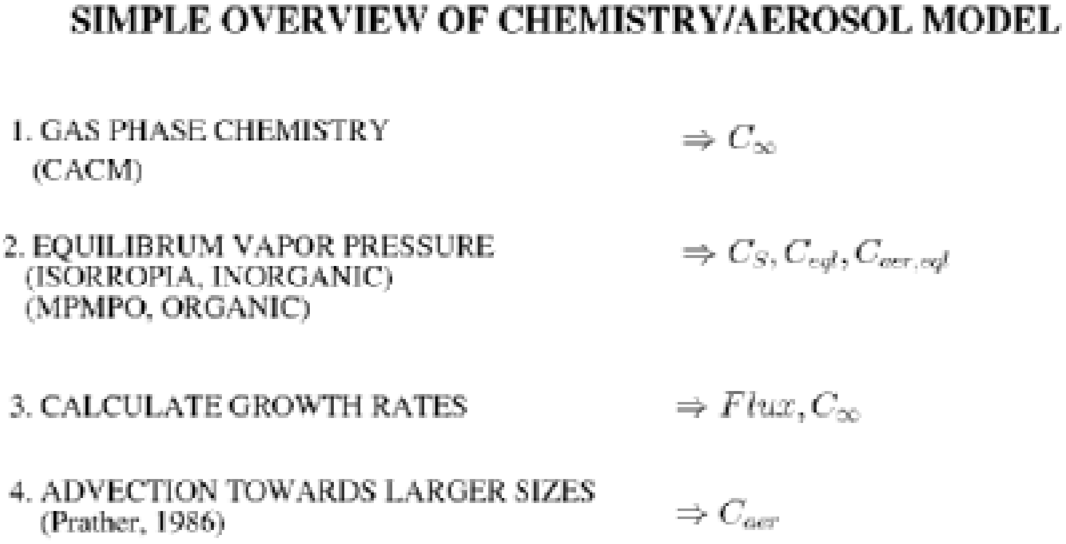


Figure 1. Illustration of condensation towards the aerosol system. At time t=0, the aerosol has concentration C_{aer}, and the gas phase has concentration C_∞. Gas phase diffusion will try to change the gas phase concentration to C_{eql}, and on the same time change the aerosol phase concentration to $C_{aer,eql}$ which are the final equilibrium concentrations. Each size bin will have it's set of fluxes depending on the gas and aerosol phase concentrations. Time scales to reach equilibrium through condensation are given by $\tau_{gas,cond}$ and $\tau_{aer,cond}$ which are equal. Additional timescales apply to the rate of change of C_S.

Figure 2 shows the structure of the box model being developed. First, gas phase concentrations are calculated using the CACM chemical model [Griffin *et al*, 2002]. Then equilibrium vapour pressures are found using the thermodynamic modules MPMPO [Griffin *et al,* 2003, Tulet *et al,* 2006] and ISORROPIA [Nenes *et al,* 1998]. Then condensation fluxes for each size distribution is calculated. These fluxes are translated to a growth rate, and particles grow to larger bins using the advection scheme of Prather [1988]. This updates the aerosol concentrations.



SIMPLE OVERVIEW OF CHEMISTRY/AEROSOL MODEL

1. GAS PHASE CHEMISTRY (CACM) $\Rightarrow C_\infty$

2. EQUILIBRUM VAPOR PRESSURE (ISORROPIA, INORGANIC) (MPMPO, ORGANIC) $\Rightarrow C_S, C_{eql}, C_{aer,eql}$

3. CALCULATE GROWTH RATES $\Rightarrow Flux, C_\infty$

4. ADVECTION TOWARDS LARGER SIZES (Prather, 1986) $\Rightarrow C_{aer}$

Figure 2. Simple overview of the box model being developed. The scheme aims at calculating accurate condensation fluxes to all sizes of both inorganic and organic species.

Results

It should be noted that this model is still in its early development phase. Therefore, the results do not necessarily reflect the results which will appear when the model is in a more stable, future version. Nevertheless, I show some examples of results below. The results are from test-simulations where 4 size bins are used, and the initial gas phase concentrations are 200 ppb of aromatics and 300 ppb of alkenes. Advection is ignored in these simulations. Nine hours are simulated. Figure 3 shows start and end volume size distribution for a simulation this test-simulation. Figure 3 shows that in these simulations, the aerosol grows mainly by adding SOA on them.

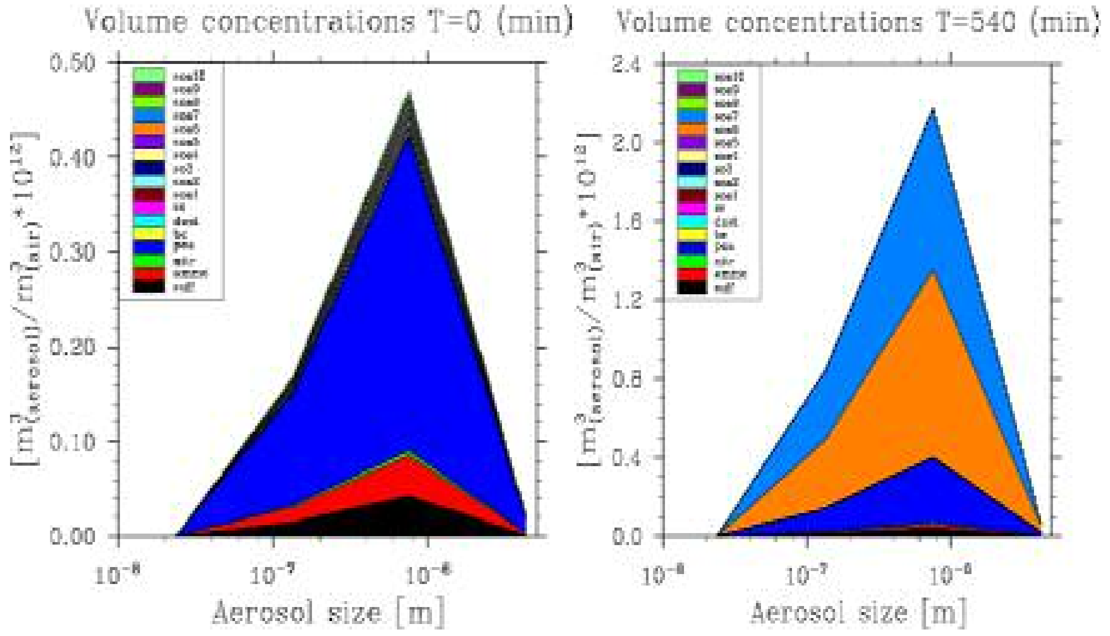


Figure 3. Volume size distribution at start of the simulation and after 9 hours when using 4 size bins. The aerosols grow mainly due to SOA being added to them.

An interesting feature of this model is that we can explicitly calculate the time scale for each bin to be in chemical equilibrium with the gas phase. In Figure 4, we show the time scale for the lumped SOA species (SOA6), to be in chemical equilibrium. The figure shows that the small particles in bin 1 reach chemical equilibrium with the gas phase much faster than the larger particles in size bin 4. The physical interpretation of this is that less mass is needed in this bin to reach chemical equilibrium (the surface area of the particle is larger per particle mass). This model can thus simulate the change slow depletion of gas phase concentration from larger aerosols and that for example gas can continue to condense on large aerosols and evaporate from smaller aerosols (see, for example, Meng and Seinfeld, [1996]).

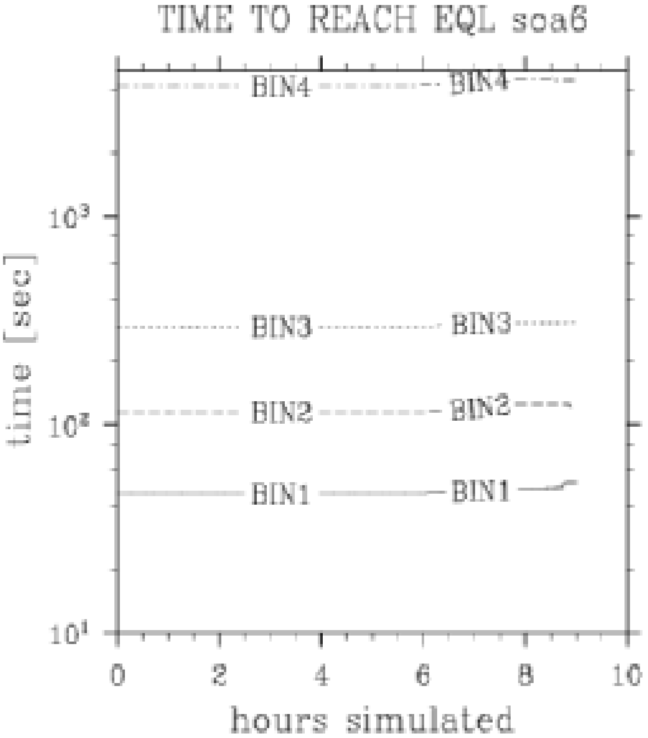


Figure 4. Time scale for the different size bins to reach equilibrium. The small particles reach equilibrium earlier than the larger particles

Future work

The model presented here, is a first version which is at a testing level. Given the relatively recent starting point of this project, there are several important aspects that are not taken into account yet and the model is still in its early development phase. The most urgent improvements are:

* make sure that growth is stable under all conditions. In some situations, equilibrium vapour pressures can change rapidly resulting in oscillations;

* calculate coagulation rates;

* use thermodynamic model of Kulmala *et al,* [2004] for the very smallest particles instead of the regular thermodynamics; and

* include formulations for nucleation rates.

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Organic Aerosol in the Global Aerosol-Climate Model ECHAM4/MADE

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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The aerosol-climate model ECHAM4/MADE enables the simulation of the global atmospheric aerosol cycles including predictions of the aerosol mass and number concentration, aerosol composition and size distribution [Lauer *et al.*, 2005; Lauer and Hendricks, 2006]. The model is based on the general circulation model ECHAM4 [Roeckner *et al.*, 1996] and the aerosol dynamics model MADE [Ackermann *et al.*, 1998; Schell *et al.*, 2001]. The aerosol size distribution is considered by three log-normally distributed modes representing Aitken (particle size < ~100nm), accumulation (particle size between ~100nm and ~1µm) and coarse mode particles (particle size > ~1µm). Aerosol components considered are sulfate (SO_4), ammonium (NH_4), nitrate (NO_3), black carbon (BC), particulate organic matter (POM), sea salt, mineral dust and aerosol liquid water.

Global climate simulations require extraordinary high numerical expenses with regard to both calculation time and memory. The consideration of aerosol microphysics and chemistry further increases the numerical costs significantly. Hence simplifications are necessary to make global aerosol-climate simulations accomplishable. Organic aerosols significantly contribute to the global aerosol, especially in the fine particle size range, and show a large variety in composition and microphysical and chemical properties [Kanakidou *et al.*, 2005]. Due to the limitations of available computational resources discussed above as well as many uncertainties in the global emissions, atmospheric fate and composition of particulate organic matter and its precursors, organic aerosols are considered in a very simplified manner in most global climate models Textor *et al.*, 2006]: the different kinds of organic aerosol compounds are represented by a single species mostly referred to as POM. This includes both primary and secondary organic aerosol compounds.

Global simulation of particulate organic matter

Figure 1 shows global POM distributions simulated with ECHAM4/MADE as a contribution to the AeroCom project [http://nansen.ipsl.jussieu.fr/AEROCOM/; Kinne *et al.*, 2006; Textor *et al.*, 2006]. The simulation considers emissions of aerosols and their precursors representative for the year 2000 [Dentener *et al.*, 2006]. The POM emissions considered include the generation of primary organic aerosol (POA) by wild-fires (global emission: 34.7 Tg/yr) as well as combustion of biofuel (9.1 Tg/yr) and fossil fuel (3.2 Tg/yr). Secondary organic aerosol (SOA) production is calculated from natural terpene emissions assuming that 15 % of the natural terpenes released into the atmosphere are transformed to SOA. This results in a global SOA production of 19.1 Tg/yr. It is further assumed in the AeroCom simulations (AeroCom Experiment B) that SOA forms on short time-scales and, therefore, SOA precursor emissions are instantaneously condensed onto pre-existing aerosol. Hence the transport and chemistry of SOA precursors is neglected in this simplified approach. It is assumed in ECHAM4/MADE that 50 % of the emitted POM is hydrophobic and, therefore, cannot be washed out by precipitation. The conversion to hydrophilic POM is parameterized as an exponential decay with an e-folding time of 24 hours.

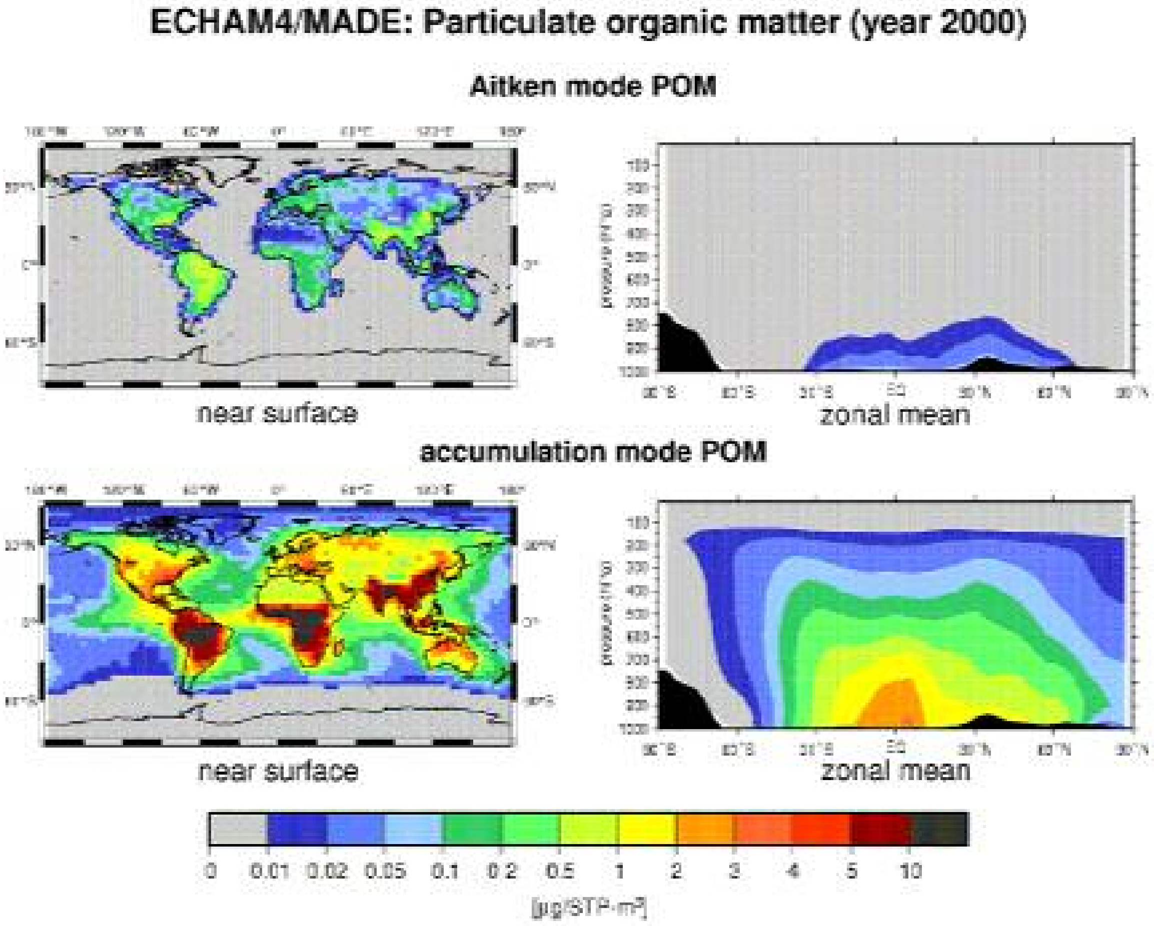

Figure 1. Climatological annual means of simulated POM (particulate organic matter) mass concentration for Aitken (top) and accumulation mode (bottom) obtained from a 10-year integration with the ECHAM4/MADE GCM [Lauer *et al.*, 2005; Lauer and Hendricks, 2006]. For each mode, the geographical distribution of the lowermost model layer (left), which is about 60 m thick, and the zonally averaged vertical cross section (right) are shown. The concentrations are given at STP (standard) conditions. The simulation considers aerosol and aerosol precursor emissions representative for the year 2000 [Dentener *et al.*, 2006].

The ECHAM4/MADE results presented in Figure 1 reveal that near surface concentrations of Aitken mode POM are largest in highly populated areas where POM is released due to combustion processes. Large concentrations of Aitken mode POM are also simulated for continental areas in the tropics where production of SOA due to terpene emissions from vegetation are most efficient. The distribution of accumulation mode POM near the surface resembles that of POM in the Aitken mode since the sources are similar. Nevertheless, accumulation mode POM shows quite high concentrations over Africa and South America. This is mainly due to wild fires which mainly release particles in the larger size mode. The simulation suggests that Aitken mode POM has a smaller average lifetime than POM in the accumulation mode. This is mainly due to an efficient transformation of Aitken mode particles into the accumulation mode driven by coagulation and condensational growth as well as more efficient dry deposition. This is clearly reflected by the horizontal and vertical dispersion of Aitken mode POM which is less efficient than in the accumulation mode.

Potential of global climate models to represent SOA

The capabilities of supercomputers are growing continuously. This will enable a more detailed representation of POM in global climate models in the future. This could potentially be realized by an individual representation of different types of POA and by an explicit simulation of SOA precursor chemistry as well as SOA formation and loss. Detailed chemistry schemes for global climate models are already available [Sander *et al.*, 2005] which could be modified to cover organic aerosol precursor chemistry. Aerosol composition including SOA compounds could by calculated by applying gas-aerosol partitioning methods as developed, for instance, by Metzger *et al.* [2002, 2005] or Schell *et al.* [2001]. Nevertheless, the comprehensiveness of chemistry schemes as well as the number of aerosol compounds considered in future aerosol-chemistry-climate models will still be limited by the computational expenses. A more detailed representation of SOA and its precursors in climate models will still require simplifications. To design such simplifications, the following questions/topics should be addressed:

1. How relevant is SOA on the global scale? How large is the contribution of SOA to the total organic aerosol? Can SOA be neglected in global climate simulations?

If SOA has to be considered further questions arise:

2. Which are the most important compounds of SOA on the global scale? Is it appropriate to reduce SOA to these compounds in global climate models?
3. Has explicit SOA precursor chemistry to be taken into account in global climate models? What are the time scales of SOA formation? Is SOA formation a sub-grid scale process in global climate models?

If the formation of the most relevant SOA compounds occurs on temporal and spatial scales smaller than the temporal / spatial resolution of the global model, SOA formation could be parameterized. This means that SOA yields from precursor emissions could be prescribed as a function of driving parameters (*e.g.* temperature, solar zenith angle, degree of pollution). Explicit SOA precursor chemistry has not to be considered in this case.

The formation of gaseous semi-volatile organics could be handled similarly if occurring on short time scales. Such compounds could be transported as inert gases until ambient conditions facilitate their conversion to SOA.

4. What are the global emissions of relevant SOA precursors? What are the corresponding SOA yields?
5. Which fraction of SOA forms new particles due to nucleation?
6. How large is the cloud scavenging efficiency of different types of SOA? How does SOA impact cloud formation?

SOA precursor chemistry has to be considered explicitly in case of the temporal/spatial scales of SOA formation being large compared to the scales of the global model. This results in the following questions:

7. Which subset of species / reactions is sufficient for the representation of SOA and SOA precursor chemistry in a global climate simulation?
8. Which fraction of SOA compounds can be handled as outlined in item 3? Which fraction has to be represented by the chemistry scheme? Which fraction can be neglected?

Acknowledgements

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Simulation of SOA Formation and Removal with the Oslo CTM2: The Importance of NO_3 for SOA Production

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Summary

A scheme to calculate the global distribution of secondary organic aerosol (SOA) has been added to the chemistry transport model OSLOCTM2. A one year model run was carried out, for 2004, and a comparison of some first results with values reported by other groups is presented. We find that the contribution of the products of monoterpene oxidation by NO_3 to the SOA burden is greater than previously reported.

Introduction

The study of atmospheric aerosol is important for many reasons, ranging from its impact on human health, to its influences on atmospheric chemistry and climate. In addition to directly affecting the Earth's radiation balance by absorbing and scattering incoming and outgoing radiation, aerosols can influence the formation, lifetime and radiative properties of clouds. Around 20-50 % of total fine aerosol mass at continental mid latitudes consists of organic matter, and this contribution can reach 90 % in tropical forested areas [Kanakidou *et al.* 2005]. In order that future changes in aerosol mass or distribution and the resultant effects can be estimated, it is important that the processes leading to the observed organic aerosol are accurately represented in atmospheric models.

Model description

The OSLOCTM2 is a three dimensional off-line CTM, with variable horizontal and vertical resolution. A horizontal resolution of T42 was used in this study, and 40 layers between the surface and 10 hPa were included. The necessary meteorological data was generated for 2004 by running the Integrated Forecast System (IFS) of the European Centre for Medium Range Weather Forecasts, and saving the 3 dimensional wind and temperature fields every three hours.

The time step used in the chemistry integration in the troposphere is 15 minutes, and the transport of species is calculated with a 15 minute time step in the boundary layer, or 1 hour in the free troposphere. As well as the new SOA scheme, the model includes calculations of the distribution of sea salt, dust, nitrate, sulphate and black carbon and primary organic aerosols.

A more thorough description of the model can be found in [Berglen *et al.* 2004].

The new SOA scheme

The SOA scheme which has been implemented in the model is based on that of Chung and Seinfeld [2002]. It will be described in more detail in an upcoming paper (JGR, manuscript in preparation), however a brief summary will be given here. In addition to the species included by Chung and Seinfeld [2002], four precursor hydrocarbons with anthropogenic sources have been added – toluene, xylene, trimethylbenzine and "other aromatics" (represented as two lumped species, as done by [Tsigaridis and Kanakidou

2003]). Isoprene was also included in the scheme based on the work of Henze and Seinfeld [2006].

Emissions

Emissions of monoterpenes and other biogenic reactive volatile organic compounds (ORVOC) are taken from the Global Emissions Inventory Activity (GEIA) data base for the year 1990, and are described by Guenther *et al.* [1995]. The emission factors of Griffin *et al.* [1999] are used to assign fractions of these emissions to 12 tracers. Total monoterpene emissions are about 127 Tg C per year, for ORVOC the total is about 260 Tg C per year, however only about 32 % of them are assumed to be able to form SOA.

The emission of monoterpenes is, for many plant species, temperature (and not light) dependent [Guenther *et al.* 1995, Kesselmeier and Staudt 1999] and can therefore also occur during periods of darkness. In order to take this temperature dependence into account, the monoterpene emissions were scaled during each month using equation 11 of Guenther *et al.* [1995], according to the local temperature, which was used as a proxy for leaf temperature. The sum of the monoterpene emissions at a particular point over a given month are kept constant during this scaling. This is different from the approach used by Chung and Seinfeld [2002], where the solar elevation was used to scale emissions, and it leads to a greater concentration of monoterpenes during the night. This in turn leads to a greater importance of NO_3 oxidation for SOA formation, given that the concentration of NO_3 is far higher during the night than during the day.

The temperature dependence of isoprene emissions was also accounted for by scaling according to local temperature, using equation 10 of Guenther *et al.* [1995], however, during the night-time, no isoprene was emitted [Kesselmeier and Staudt 1999].

Emissions of primary organic matter are based on the inventory of Liousse *et al.* [1996] and emissions of aromatic SOA precursors are taken from the files produced in the REanalysis of the TROpospheric chemical composition over the past 40 years (RETRO) project [Schultz *et al.* manuscript in preparation].

Oxidation and partitioning

The oxidation of the precursor hydrocarbons and subsequent gas/particle partitioning of the oxidation products is described by means of a two product model [Hoffmann *et al.* 1997]. Reaction rates for the oxidation of monoterpenes and ORVOC, as well as the mass based stoichiometric coefficients and partitioning coefficients are as described in Chung and Seinfeld [2002], for isoprene the equivalent values are taken from Henze and Seinfeld [2006] and for the anthropogenic aromatic SOA precursors, reaction rates are as in Tsigaridis and Kanakidou [2003], while the stoichiometric coefficients and partitioning coefficients are from Odum *et al.* [1997].

Partitioning is assumed to occur into all existing organic aerosol.

Removal

A dry deposition velocity of 0.1cm s^{-1} is applied to all SOA in the lowest model level [Liousse *et al.* 1996].

Rain-out via convective precipitation as well as large scale precipitation is accounted for, with 80% of the SOA dissolving into cloud droplets when these are present. A temperature dependent Henry's law coefficient of $H=1 \times 10^5$ M atm^{-1} is used to calculate the solubility of the gas phase oxidation products [Chung and Seinfeld 2002] while 1×10^3 M atm^{-1} and 1×10^4 M atm^{-1} are used for the oxidation products of the aromatic species and the first product of xylene oxidation respectively [Tsigaridis and Kanakidou 2003]. The monoterpene and ORVOC species are also subject to wet removal, albeit for these species a very minor process.

Simulation

The model was spun up for four months, and then allowed to run for the whole of 2004. All precursor hydrocarbon, gas phase oxidation product and aerosol species were transported. The oxidation of precursor hydrocarbons and the partitioning to the aerosol phase was calculated for the whole troposphere, and the total net production and burden were saved. The three dimensional instantaneous fields for all the SOA relevant tracers were also saved every three hours.

Results

The monthly mean total column amount of SOA for August is shown in Figure 1. As expected there are peaks over South America, Africa and Europe, as well as parts of Asia and North America.

The total net production of SOA during 2004 was 51.5 Tg, calculated as the sum of partitioning to the aerosol phase, minus partitioning from the aerosol phase back into the gas phase, over the whole year. The annual average burden was about 0.4 Tg. Both of these figures are within the range of the findings of previous studies, for example Tsigaridis and Kanakidou [2003] give a production of 2.5 – 44.5 Tg yr^{-1}, when only biogenic precursors are considered, with a contribution of between 0.05 and 2.62 Tg yr^{-1} resulting from the inclusion of anthropogenic precursors. An annual total production of 64 Tg yr^{-1} is found by Derwent *et al.* [2003], and Chung and Seinfeld [2002] calculated an SOA production of 11.2 Tg yr^{-1}, with an annual average burden of 0.19 Tg.

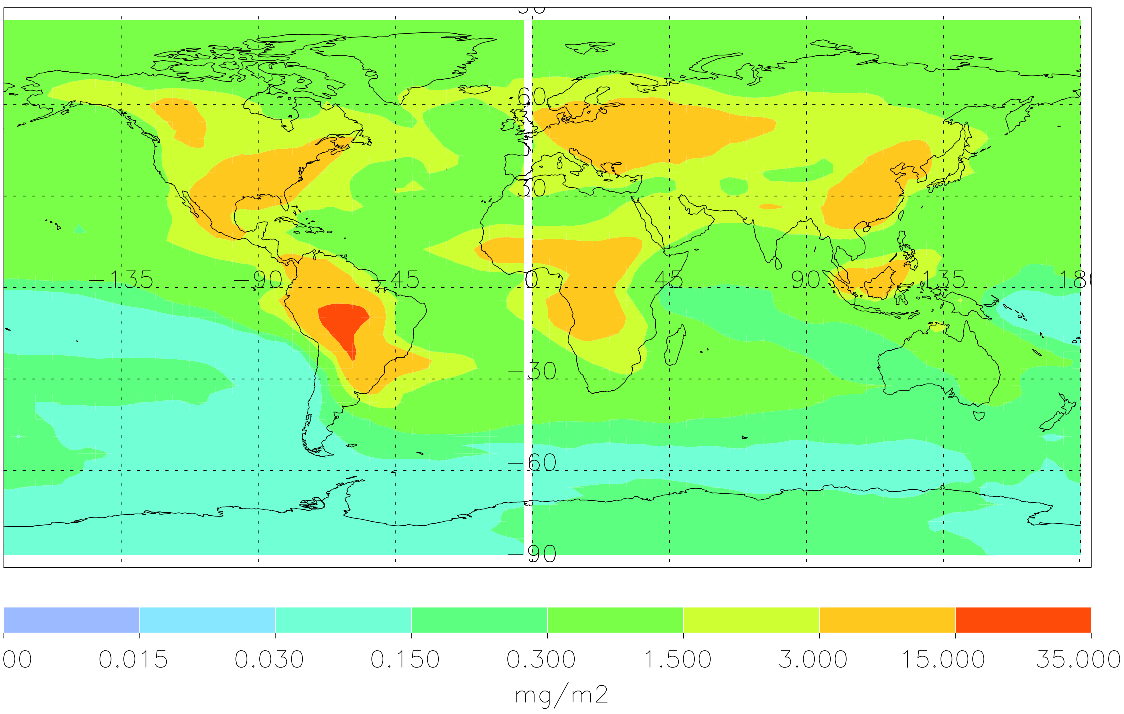

Figure 1. Monthly mean distribution of total column SOA for August 2004.

One of the reasons that the total production and average burden are higher in the present study than in that of Chung and Seinfeld [2002], on which our SOA scheme is based, is the inclusion of SOA formation resulting from isoprene oxidation. It was suggested by

Claeys *et al.* [2004] that isoprene oxidation by OH could lead to formation of significant amounts of SOA. In a recent study by Henze and Seinfeld [2006], isoprene was included as a precursor for SOA. Considering only the oxidation of isoprene by OH, they found the additional source to lead to more than a doubling of the global burden of SOA. As well as directly forming more SOA, the oxidation products of isoprene were found to enhance the production of SOA from the other precursor species by 17 %. In the present study, it was found that the SOA formed from the oxidation products of isoprene contributes 28 % to the annual global burden. The enhancement of SOA formation from other species has not yet been assessed.

As well as the additional SOA source from the inclusion of isoprene in this study, anthropogenic precursor gases contribute 4 %, to the annual global burden (a total annual production of 2.6 Tg yr^{-1}).

The annual average lifetime of SOA was calculated to be 2.8 days, which is significantly shorter than the 6.2 days given by Chung and Seinfeld [2002]. As the major loss process for SOA in both studies was calculated to be wet deposition (here it was found to be 94 % on average for 2004) and the same solubility was used for SOA, the difference probably lies in the calculation of convection and precipitation in the models. The annual mean lifetimes of different species range between about 2.2 and 4.1 days, with one of the oxidation products of isoprene having the longest lifetime.

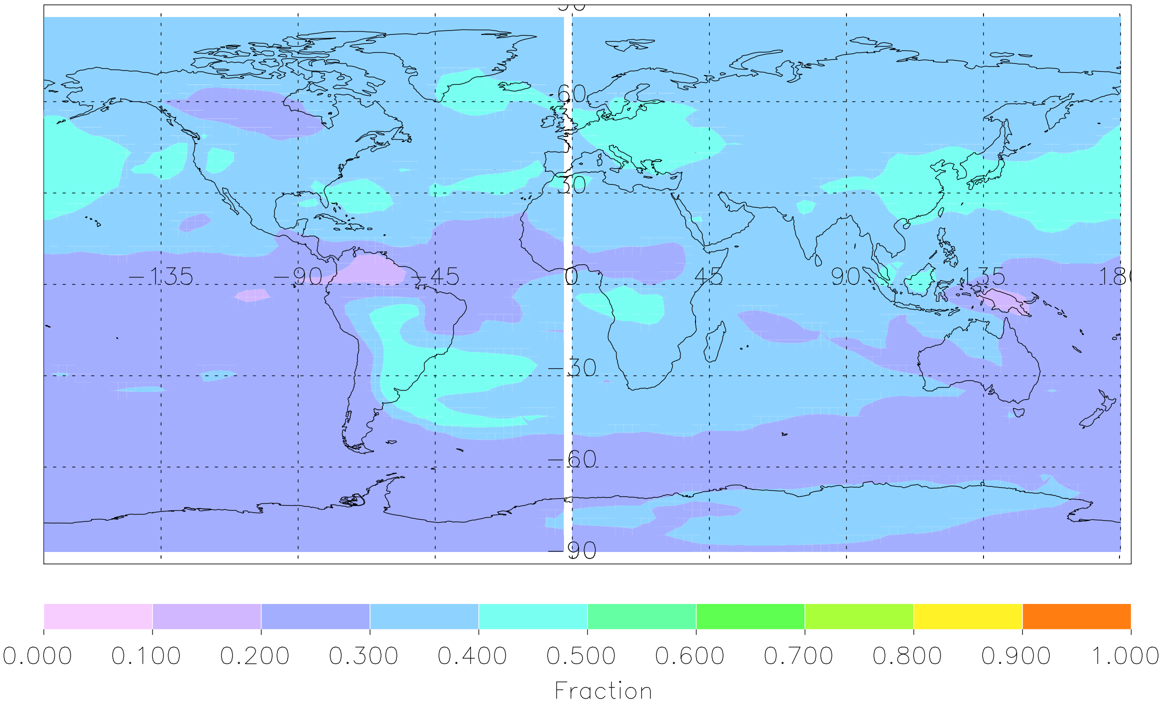

Figure 2. Monthly mean fraction of total SOA column mass which is composed of NO_3 oxidised species, August 2004

One of the differences between the SOA scheme used in the present study, and that of Chung and Seinfeld [2002], as mentioned above, is the way the monoterpene emissions are scaled. This results in an increased importance of the NO_3 oxidation products for the total mass of SOA produced. The fraction of the total SOA which is formed from NO_3 oxidation products varies significantly with location, as is shown in Figure 2. As much as 40 % to 50 % of the total column mass of SOA over areas such as central and eastern Europe, eastern Asia and parts of south-east Asia as well as South America is composed of NO_3 oxidised compounds. A comparison with Figure 1 shows that these regions are also those where the total mass of SOA is especially high, therefore NO_3 oxidation products make up a significant fraction of the global burden. In fact, for 2004, the model predicts that around 32 % of the annual average global burden of SOA consists of NO_3

As many of the regions where NO_3 oxidation has the largest contribution to SOA formation are in heavily populated areas, the anthropogenic influence on NO_3 levels may have a significant impact on SOA formation.

Future outlook

Further model simulation are planned in order to simulate SOA distributions in pre-industrial conditions. Some uncertainties that will be looked at in the future include the ageing of hydrophobic primary organic aerosols (POA), and their conversion to hydrophilic species. The timescale over which this ageing occurs is uncertain, and will have an impact on the wet deposition rates of POA. A further experiment will be carried out to investigate the impact of model horizontal resolution on the calculated SOA production and burden. With respect to the importance of NO_3 oxidation of monoterpenes for SOA formation, one of the main uncertainties comes from the distribution of different plant species. There are many species which do not emit monoterpenes during periods of darkness; therefore the importance of NO_3 for SOA formation calculated here is probably an upper limit. In the future, the contribution of NO_3 could be better constrained by taking the distribution of different plant species into account when calculating the light dependence of monoterpene emissions. This would require a global, gridded data set providing the appropriate information about the composition of the plant population within each grid box.

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The Atmospheric Oxidation of Volatile Organic Compounds and Formation of Secondary Organic Aerosol: The Need for Complex Mechanisms

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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The atmospheric oxidation of volatile organic compounds (VOCs) leads to the production of oxygen-containing more polar molecular products which may be of sufficiently low-volatility to transfer from the gas phase to a condensed organic (*i.e.* aerosol) phase. Where in the gas phase the distribution of oxidised organic molecules reflects their *in situ* relative formation rates, in the aerosol phase the distribution of oxidised carbon is further strongly weighted by specific physical (*e.g.* volatility) and chemical properties (*e.g.* propensity to undergo "stabilising" accretion reactions). This means that an oxidation product that is only considered to be "minor" in the gas phase may be very significant for the formation and growth of secondary organic aerosol (SOA) material. Thus there is a need for detailed understanding of the oxidation of VOCs that may lead to the significant production of SOA in the Earth's atmosphere.

Introduction

The oxidation of VOCs, of both anthropogenic and biogenic origin, is generally initiated through reactions of the radicals $^{\cdot}OH$ and NO_3, and of O_3 [Kanakidou *et al*, 2005]. In terms of the ability to form SOA material, it is generally accepted – although there do appear to be exceptions – that a VOC must contain at least six carbon atoms and that the major anthropogenic and biogenic precursors to SOA material are aromatic hydrocarbons and mono- (and sesqui-) terpenes, respectively. In the former case, oxidation is initiated by reaction with $^{\cdot}OH$ (giving rise to a hydroxycyclohexadienyl-type radical which can add molecular oxygen before undergoing a complex series of reaction giving both ring-retaining and ring-fragmented products) and in the latter, ozonolysis reactions (in which the initially formed primary ozonide adduct decomposes to give a carbonyl and a carbonyl oxide, this latter further decomposing to give oxygen-containing products) produce SOA most readily. Both of these chemistries are complex and far from fully elucidated.

Further complexity is realised when considering that (secondary) organic aerosol yields that have been measured for such species in chamber studies were obtained under conditions which may be far from those encountered in the real atmosphere. Furthermore, it is becoming increasingly clear that molecular-weight building association (so-called "accretion"-) reactions are serving to stabilise oxidised organic compounds once they have transferred from the gas phase to the aerosol. Which types of association reaction (Figure 1) are most important in this latter respect is unclear – *i.e.* which structural moieties of the reacting molecules, or which combinations of functional groups, give rise to the most efficient production of stable, higher molecular weight adducts is not known. Once a clearer idea of such stabilising chemistry has been formed, focus can be placed on understanding the specific – perhaps relatively-minor – pathways in the complex gas-phase oxidation chemistry which give rise to the formation of species feeding this chemistry. If, for example, one type of association chemistry predominates this will be reflected in the distribution of functionalities (most notably, non-C-C bond molecular linkages) observed in aerosol oligomeric material – of laboratory and atmospheric origin.

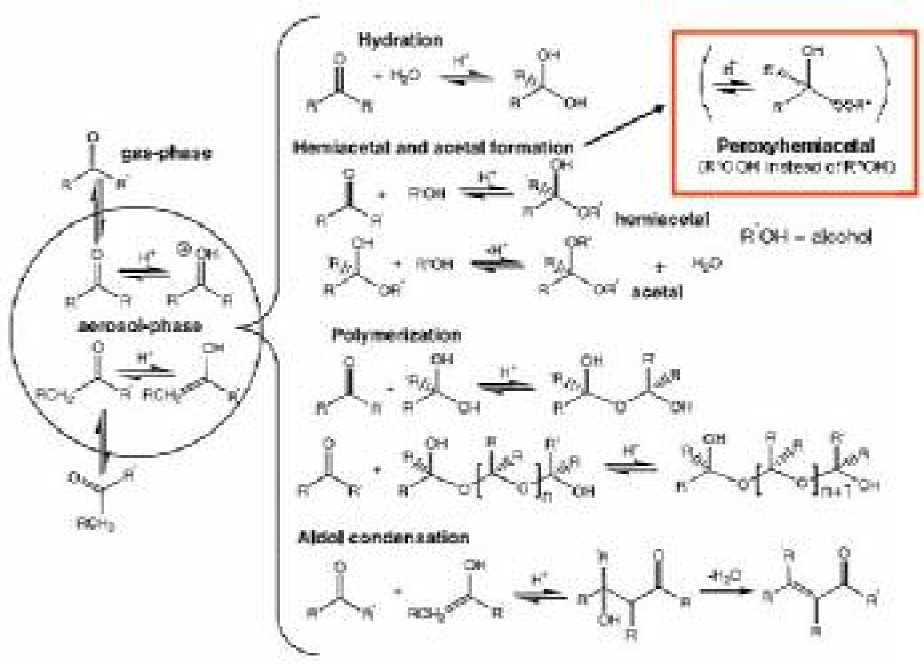

Figure 1. Acid-catalysed heterogeneous reactions of atmospheric carbonyls. Figure reproduced from the published study of Jang *et al.* [2002].

Scientific activities

In order to begin to better understand which aspects of the mechanism of oxidation of aromatic hydrocarbons influence the formation of SOA, Johnson *et al.* [Johnson *et al.*, 2004; Johnson *et al.*, 2005] compared aerosol yields measured in sunlight-driven, ·OH-initiated oxidation experiments, at the European Photoreactor in Valencia, for a number of different aromatic precursor species. By comparing aerosol yields (expressed on a mass basis) measured at a stated total organic aerosol mass loading – partitioning is influenced by the amount of organic absorbent available – some aspects of the chemistry driving SOA formation and growth could be identified.

On a global scale, the production of SOA from the ozonolysis of terpene species is extremely important. The Criegee mechanism of ozonolysis is complex and incompletely understood [Calvert *et al.*, 2000], in great part due to uncertainty in the chemistry of carbonyl oxide (so-called Criegee) intermediates. Work recently carried out in the University of Reading [Yan Ma, 2006] measured the formation of specific organic diacid products from the ozonolysis of α-pinene in the presence of ·OH-radical scavengers (·OH is a product of this chemistry) and showed that these yields varied with the nature of the scavenger(s) added. These observations were rationalised in terms of the effects of varying amounts of $RO_2^{\cdot}$ and $HO_2^{\cdot}$ (produced from the ·OH-scavenging chemistry) on the radical chemistry giving rise to the formation of the acids.

Scientific results and highlights

In Figure 2, the dependence of SOA yield on the amount of NO present can be seen for the case of toluene photo-oxidation. It is clear that as the amount of NO available is reduced, the efficiency with which SOA can be formed is increased.

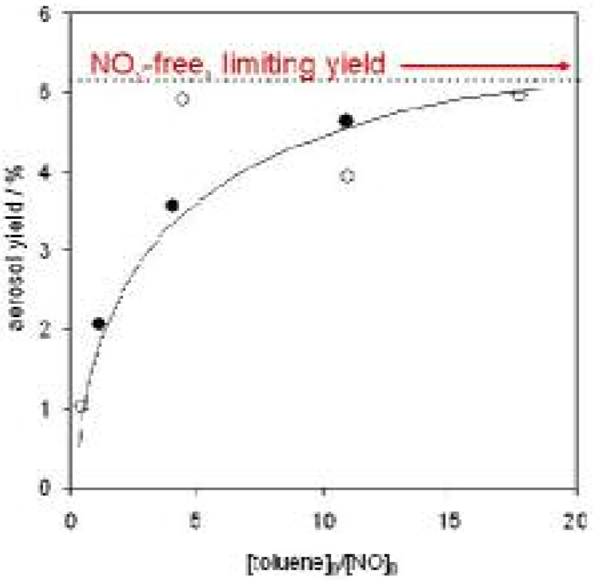

Figure 2. Variation in aerosol yield (measured at 50 μg m^{-3} organic aerosol mass loading) with initial toluene to NO concentration.

This is consistent with a greater contribution to SOA material of products derived from the reactions of organic peroxyl radicals (RO$_2^{\cdot}$) with, for example, the hydroperoxyl radical (HO$_2^{\cdot}$). The products of such reactions are organic hydroperoxides which may participate in accretion reactions.

Figure 3 contains SOA yield data, measured at a stated organic aerosol mass loading and aromatic precursor to NO concentration ratio, for a series of different aromatic species. These yields are seen to vary systematically with the amount of unsaturated aldehyde species predicted to be formed from ring-fragmentation reactions. Thus, although chamber experiments may not be very representative of real atmospheric conditions, they can provide some very useful "clues" as to which compound-types are important for SOA formation.

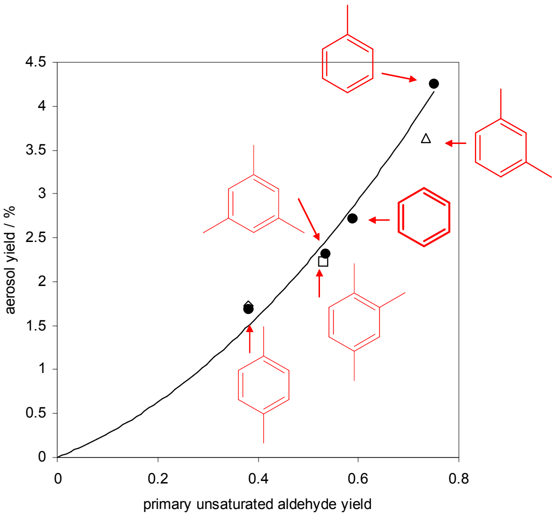

Figure 2. Variation in aerosol yield with primary yield of unsaturated aldehyde species from ring fragmentation.

What the data in Figures 2 and 3 suggest are that association reactions occurring inside the growing aerosol play a key role in determining SOA formation efficiencies. The types of association reaction likely to be playing a role all involve acid catalysed reactions carbonyl species including acetal, hemiacetal and peroxyhemiacetal formation; polymerisation (or oligomerisation) and aldol condensation. Which of these reaction types are the most important, in general or specific cases, is not clear at this time.

Future outlook

One area of work currently being pursed at the University of Reading is to look at the effects of different ·OH radical scavengers on the yields of adipic acid (C_6-dicarboxylic acid) and glutaric acid (C_5-dicarboxylic acid) from the ozonolysis of cyclohexene. This is a simple, symmetric analogue for α-pinene. By numerically simulating such reaction systems the feasibility of proposed ozonolysis mechanisms – incorporating current understanding of organic radical chemistry – can begin to be tested. Such a mechanism – specifically for the formation of oxidation products, including glutaric acid – has recently been presented by Ziemann [2002] and is reproduced in Figure 4.

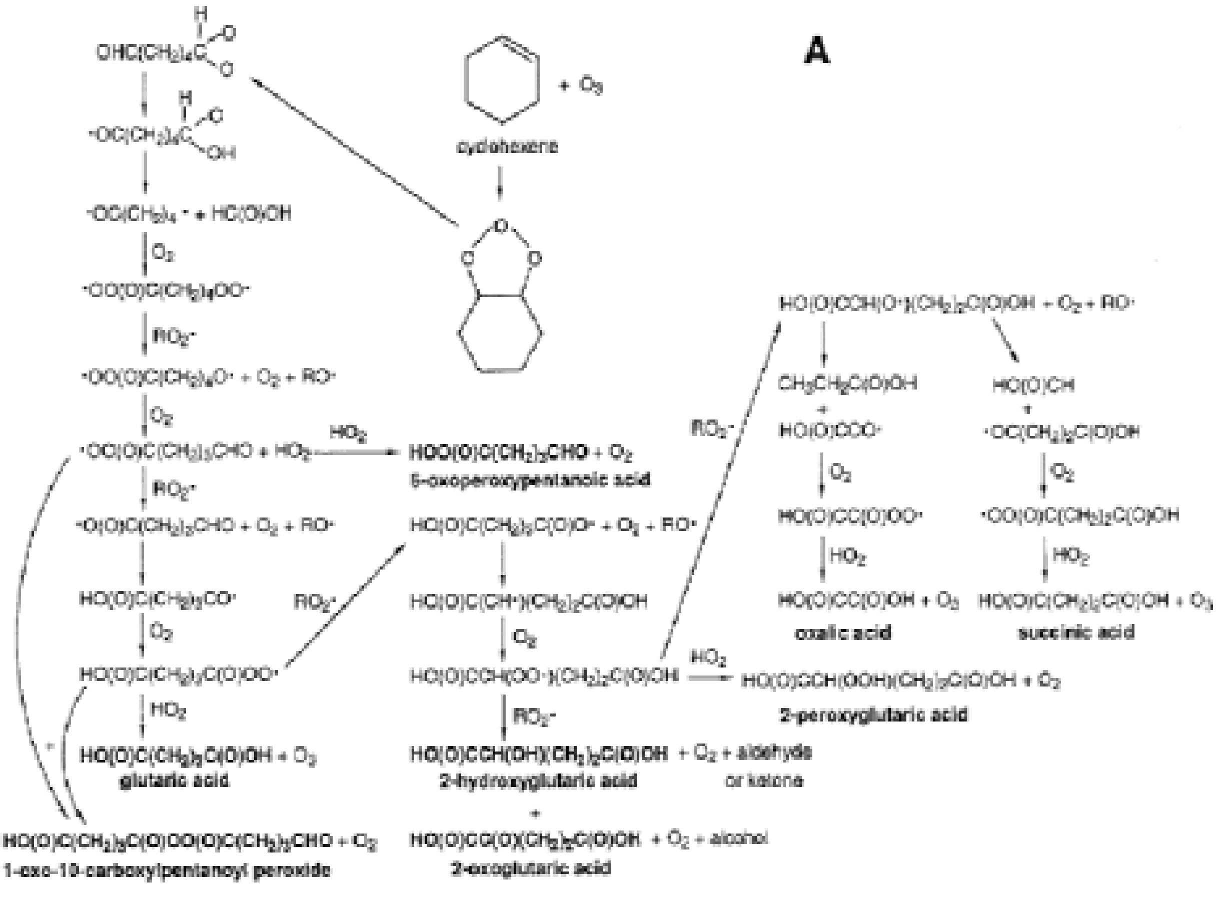

Figure 3. Proposed ozonolysis pathways leading to glutaric acid and other reaction products.

That other decomposition fates are available to the cyclohexene Criegee intermediate (*i.e.* decomposition fates other than the ·OH-forming hydroperoxide channel) is clear to see in Figure 5. Here, the variation relationship between, so-called, stabilised Criegee intermediate (*i.e.* able to participate in bimolecular reactions) and the measured yield of ·OH is different from that for simple acyclic alkenes.

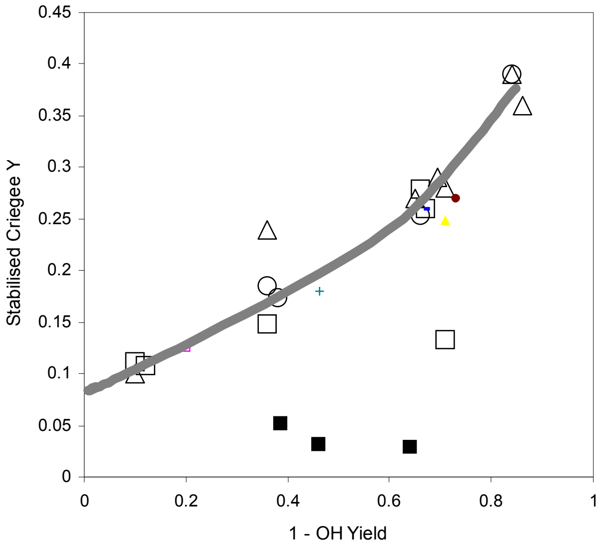

Figure 4. Variation of yield of stabilised Criegee intermediate with yield of ·OH radial. Open circles correspond to the data of Hatakeyama and co-workers [Hatakeyama and Akimoto, 1990], open triangles correspond to the data of Paulson [Hasson *et* al., 2001a; Hasson *et al*., 2001b] and co-workers and open squares correspond to the data of Rickard *et al.* The filled squares correspond to the data of Hatakeyama for (from left to right) cyclopentene, cyclohexene and cycloheptene.

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Molecular Properties of Secondary Organic Aerosol

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Summary

The physical and chemical properties of secondary organic aerosol (SOA) are rather poorly understood and have tended to be determined on a macroscopic rather than molecular level. It has been established that the atmospheric degradation of volatile organic compounds leads to the production of condensable more oxygenated species but that the presence of organic material in aerosol is not adequately explained simply by vapour pressure partitioning of these compounds. Studying SOA content at a molecular level gives some indication of certain key building blocks which are incorporated into lower vapour pressure oligomers. By studying oligomer and building block structures gives insight into possible in-aerosol chemistry which may be occurring, and offers some prospect that such processes may be treated in an explicit manner in the future.

Introduction

The composition and properties of secondary organic aerosol remain a major environmental uncertainty. Our understanding of how SOA varies under a variety of atmospheric conditions, for example biogenic influenced, urban, biomass burning etc, has made some major steps forward in recent years, helped in large part by techniques such as on-line aerosol mass spectrometry. The key initiation steps in SOA formation are also well accepted - that atmospheric oxidation via OH, O_3, or NO_3 of volatile organic compounds leads to more oxidised species which may have a greater propensity to partition to the condensed phase of existing aerosol, or indeed if concentrations are high enough to self nucleate. Partitioning oxygenated products of VOC to the condensed phase does not however typically transfer sufficient mass of organic when compared to observations and this has required unsatisfactory model fixes, boosting partition coefficients to move more material into aerosol. Observations within smog chambers have recently illustrated that relatively high molecular weight (and hence low vapour pressure) organic compounds could be found in aerosol, and that the size of such species grew with aging of the aerosol. Precursors studied include 1,3,5-trimethyl-benzene, cyclo-alkenes, α-pinene and glyoxal [Kalberer *et al.*, 2004; 2005; Gao *et al.*, 2004; Bahreini *et al.*, 2005; Hastings *et al.*, 2005]. This effect of mass adding reactions offers a convincing explanation of the relatively high loading of organics in aerosol when compared to the volatility of the initial VOC oxidation products. Whilst molecular weight has been extensively characterised in smog chambers, the molecular structures are less certain, and yet hold the key to understanding the mechanisms by which such oligomers may be formed.

The organic composition of aerosol is however enormously complex and without doubt on a par with biological chemical complexity. In excess of 10000 relatively volatile organic compounds can been seen within typical urban particulates [Hamilton *et al.* 2004], but even this large ensemble is seen to comprise only a very small fraction of the total aerosol mass. The complexity of small oxygenated compounds observed in aerosol reflects the diversity of products formed when VOCs are oxidised and this has lead to organic aerosol composition being typically described either in terms of macroscopic properties or as mixtures of operationally defined surrogates. A common description of secondary organics within aerosol is that they are ‘humic like’ – and whilst this conveys a reasonably good description of bulk properties, it tells us nothing about how such compounds were formed or their original precursor source. Understanding the structures of larger oligomer type molecules in aerosol is in its infancy, but since these species may well hold the key to describing organic mass, they deserve particular attention. Although a vast range of precursor condensable products are formed when even only a single VOC is oxidised, a hypothesis may be that not all such precursors will participate in mass adding reactions that form the majority oligomers, and that on a molecular level the range of larger molecules found in aerosol be somewhat simpler than the small molecule composition.

Scientific activities

Here we report attempts to elucidate structures of organic compounds found in aerosol from lab studies and smog chamber experiments. The approach used is to determine the distribution of small molecules or ‘building blocks’, and then to look subsequently at the structures of larger oligomer material to see if links can be made back to the observed building blocks. Combinations of experimental approaches are used in this study. For small organic compounds in aerosol, we place µg quantities of aerosol or study matrix directly into a thermal desorption stage and then separate the resulting volatilised mixture using two dimensional gas chromatography with time-of-flight mass spectrometry (GCXGC-TOF/MS). For larger or more polar compounds we use combinations of liquid chromatography with ESI and APCI ion trap mass spectrometry, and LC-high mass accuracy time-of-flight mass spectrometry.

Figure 1 illustrates a typical GCxGC-TOF/MS characterisation of small organic compounds found in aerosol formed from the ozonolysis of cyclohexene [Hamilton *et al* 2006]. Around 30 different small oxidation products can be found in the aerosol formed, and some key structures are shown in Table 1.

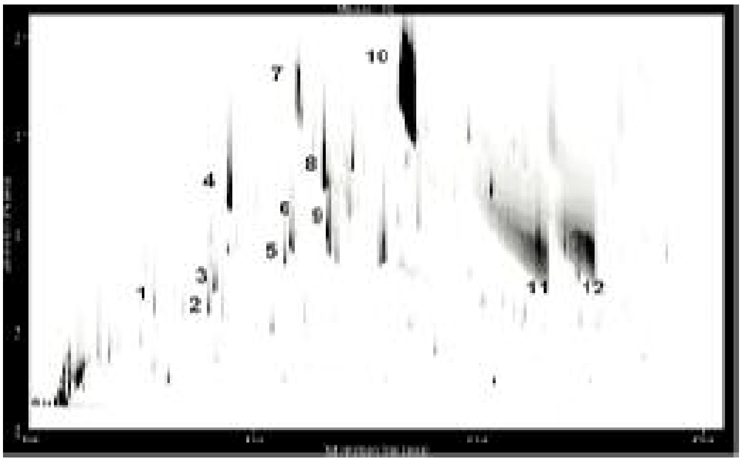
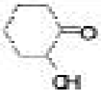
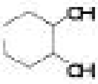
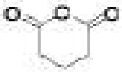


Figure 1. GCXGC chromatogram of SOA formed during cyclohexene ozonolysis. x-axis increasing boiling point, y-axis increasing polarity, z – intensity.

Such an analysis ‘misses’ the majority of the aerosol organic mass however, and a second approach is applied using HPLC to isolate individual products, and collision induced dissociation mass spectrometry to determine oligomer structures.

Table 1. Compounds identified in cyclohexene-O_3 SOA from Figure 1.

1	Butanoic acid		2	Cyclo-hexanol	
3	Cyclo-hexanone		4	Butyrolactone	
5	2-hydroxy-cyclo-hexanone		6	1,6-hexanedial	
7	2,5-furandione		8	Tetrahydro-2H-pyran-2-one	
9	Cyclohexane-1,2-diol		10	Dihydro-2H-pyran-2,6(3H)-dione	
11	Glutaric acid (Pentanedioic acid)		12	Adipic acid (hexanedioic acid)	

When the same cyclohexene aerosol system is characterised using LC approaches the products formed fall relatively cleanly into two categories of monomer or ‘building block’ material seen also using GCxGC-TOF/MS and larger dimer and trimer molecules. By retaining the parent ion from each LC peak, allows sequential ionisations to be performed (up to MS^4 typically) and some potential structures for such dimers can be extracted. Figure 2 illustrates this division between building blocks and products, and shows a typical dissociative MS spectra with two possible structures.

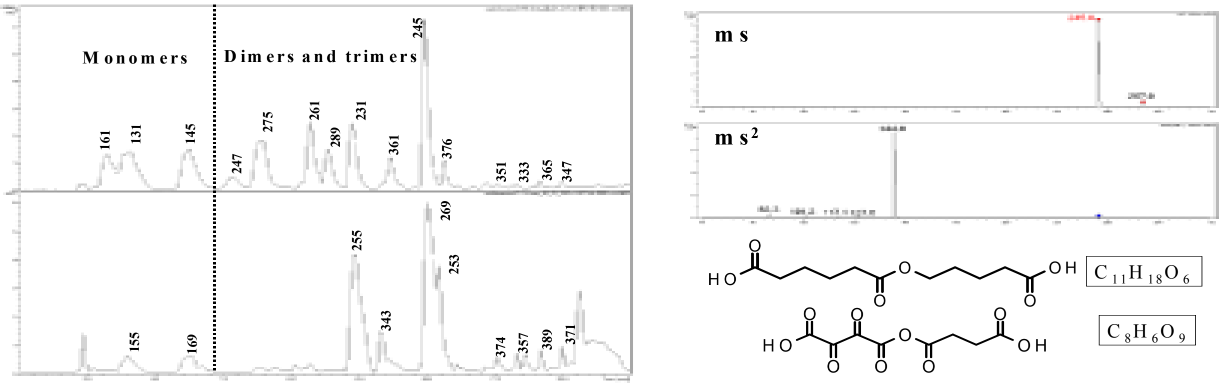


Figure 2. Left: HPLC separation of cyclohexene-O_3 SOA. Peaks labelled with most abundant ion. Right: Typical MS and MS^2 spectra and possible dimer structures that fit fragmentation patterns.

In many cases the dissociative MS does not result in a single structural possibility and it requires further analysis using LC with high resolution MS to determine the molecular formula. The combination of such data is very powerful however and allows for the majority of dimer type species to be structurally resolved (see [Hamilton *et al.,* 2006] for full details). The types of structures resolved is not limited to dimers however and there is good evidence from this and many other studies that much larger molecules may be formed in aerosol. The approach used above can be similarly applied to systems where there are multiple combinations of building blocks. A laboratory study of the oligomers formed from the ozonolysis of oleic acid indicates structures as large as 1000 Da.

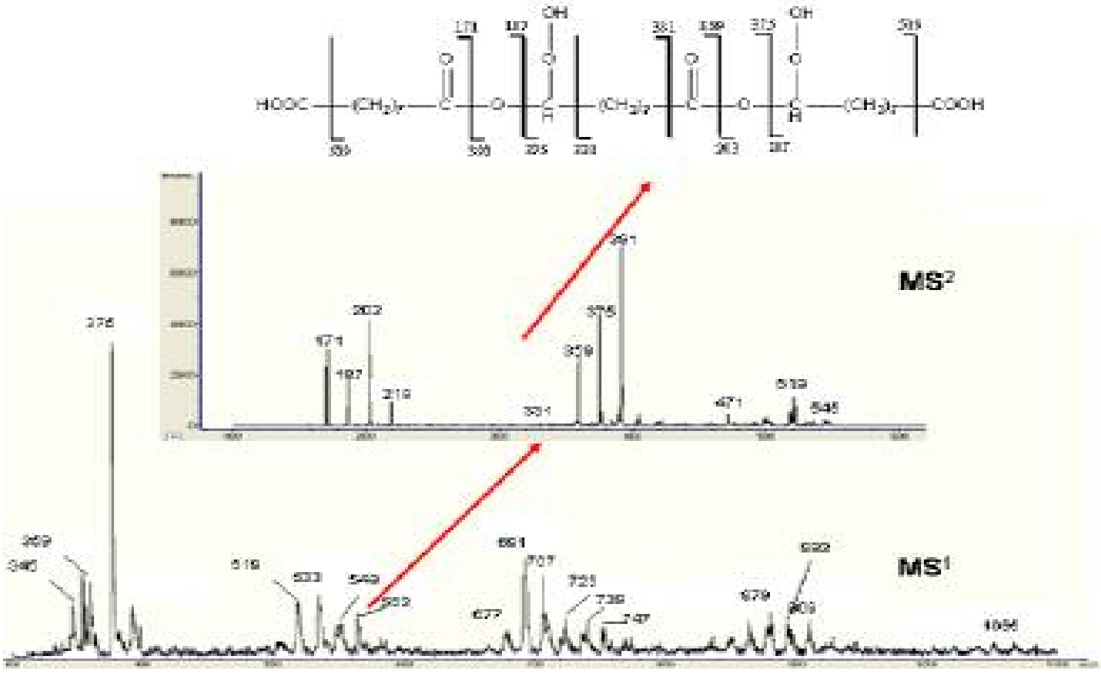


Figure 3. Ion trap MS spectra of oligomers formed from oleic acid ozonolysis. Inset is a MS2 ionisation of the 563 Da oligomer, and the derived molecular structure (and fragmentation) shown above [Reynolds *et al.,* 2006].

Figure 3 illustrates that the oligomers formed in organic aerosol can be potentially very large, but as in the cyclohexene example can be rationalised in terms of combinations of a reasonably small subset of building block compounds.

Scientific results and highlights

The organic composition of aerosol is without doubt highly complex and when even a single species is studies in a smog chamber a vast range of small carbonyls are found within the condensed phase. Many of these species are highly volatile and it remains a major uncertainty as to how their inclusion can be explained given known vapour pressures. Around 30 different small molecules could be resolved in the case of cyclohexene aerosol, but this number rises to in excess of 200 for the OH + Toluene reaction system. Using LC techniques to separate the larger organic molecules found in the resulting aerosol from this study leads to a somewhat smaller distribution of low vapour pressure products. In the case of cyclohexene, the majority of dimer and trimers observed could be explained *via* the combinations of certain small acids, all of which would be predicted as oxidation products by a comprehensive mechanism such as the MCMv3. The change in vapour pressure once the dimer is formed is stark; from 15×10^{-3} Torr for adipic acid, which we identify to be a key building block, to 7.7×10^{-8} Torr for the dimer of hydroxy pentanoic acid + adipic acid. For this particular precursor chemical, esterification reactions appeared to be the dominant mechanism resulting in oligomers, although this will by no means be the universal route to large products. In the case of large molecules formed from oleic acid ozonolysis we observe that oligomer structures can be rationalised as being combinations of the four major oxidation products and Criegee intermediates.

Future outlook

Our conclusion here is that although the chemistry that forms large apparently stable molecules in aerosol is both complex and poorly understood, the prospect of producing explicit mechanisms for their formation is not out of scope. In the, albeit, very few cases that have been examined in detail to date (and with all the caveats that using smog chambers and organic rather than aqueous phase aerosol that entail), there appear often key building block species which have propensity to undergo mass adding reactions. The complexity of large molecules formed in aerosols appears somewhat simpler in terms of compound types than the small molecules derived directly from gas phase oxidation. There is some potential therefore that only a subset of oxidation products predicted from gas phase mechanisms need to be carried forward for consideration as major players in in-aerosol reactions. Clearly however there is a vast amount of work to do in characterisation of molecular structure and from these structures, in determining reaction pathways. In addition analytical technology is currently not yet capable of working with the low concentrations and higher mixture complexity of real atmospheric aerosol. Nonetheless despite both of these readily identified limitations and challenges, we consider that a framework for SOA treatment on a molecular rather than macroscopic level can at least be conceived.

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Condensed Phase Atmospheric Organic Material

Contribution to the ACCENT workshop on volatile organic compounds: Group 3

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Summary

A significant fraction of atmospheric particulate material is almost invariably organic. The organic fraction has been relatively well-studied in recent years, but the origin and processes dominating its formation remain elusive despite the best research efforts. The organic aerosol (OA) burden is generally significantly under predicted owing largely to our inability to capture the behaviour of secondary organic aerosol (SOA). The major uncertainties in the contribution to SOA formation result from several sources. Firstly, the relative contributions from biogenic and anthropogenic precursors (and hence the geographical distribution) is unclear and the dominant parent species within each broad classification entirely unknown. The second major uncertainty results from lack of knowledge of the broad mechanisms dominating partitioning of the precursors between the gaseous and condensed phase. Conventional modelling approaches have frequently attempted to predict partitioning as a reversible absorptive process, using smog chamber data to derive the equilibrium partitioning coefficients. Although recent laboratory and chamber data results indicate stabilisation of particulate organic material by condensed phase reactions, the roles of such reactions in the real atmosphere are unclear. Higher molecular weight compounds are found in chamber experiments investigating particles self-nucleated from organic vapours from single parent VOCs and such compounds will inevitably be of low volatility. Multifunctional higher molecular weight compounds are also found in atmospheric SOA. However, correspondence between the exact mechanisms operating in the chamber and the atmosphere is unlikely since self-nucleation of organic vapours has not been observed in the atmosphere and condensed phase reactions will be concentration dependent. The atmosphere is moist and most particles will carry water in a moist atmosphere (particularly since they will generally have both inorganic and organic components). It is therefore necessary to represent SOA formation under realistic atmospheric conditions by considering all the processes likely to play a role in order to understand the mechanisms dominating the partitioning of atmospheric organic compounds.

Introduction

Atmospheric particulates are the focus of vigorous and extensive current investigation due to their roles in climate change through direct and indirect radiative forcing and to their impacts on human health. The climatic implications depend critically on the number of aerosols, their composition and resulting affinity for water in the sub-saturated environment and their ability to activate into cloud droplets moving into supersaturation. Since organic compounds are found extensively in atmospheric particles, they may be expected to play a significant role in both health and climate issues.

In contrast to atmospheric gas phase processes, the understanding of the cycling and implications of atmospheric aerosols is relatively young and underdeveloped. This is largely due to the complexity of the coupling between the microphysics and chemistry. Such complexity is evident in the understanding of the roles of aerosol particles in the carbon cycle. Fine organic particulate material is formed from partitioning between gaseous species and pre-existing particles, probably with significant water content. This is because the atmosphere is moist and a particle's water activity will be approximately equal to the relative humidity under sub-saturated conditions and only pure inorganic particles will exhibit deliquescence / efflorescence behaviour. At present, there is no evidence for self-nucleation of organic vapours in the atmosphere. The partitioning of organic components will depend upon the difference between the partial pressure of the direct gaseous precursor and the vapour pressure of this species above each particle. This will depend on the composition of the particle (determined by the product of the pure component vapour pressure and the activity of the component in the particle). Condensed phase reactions, consuming the original condensing organic species (and likely yielding lower volatility, higher molecular weight compounds) would effectively reduce its vapour pressure leading to an increased vapour mass flux towards the particle. Mass flux of the vapours will lead either to particle growth or shrinkage by condensation or evaporation. The instantaneous unique distribution of organic components across the sizes will result from partitioning to the multicomponent distribution taking into account the above processes. Whilst equilibration of fine aqueous aerosol particles of less than a few hundred nanometres will be rapid, larger accumulation mode and coarser particles will be subject to diffusional limitation to mass transfer. It is in no way straightforward to establish whether a measured aerosol organic loading is in equilibrium with a gas phase precursor owing to the complexity of the processes involved, particularly when close to sources of the gaseous species.

The condensing organic species will either be directly emitted (in which case the organic aerosol will probably be observed as primary "POA") or will result from the oxidation of a parent VOC by ozone, the hydroxyl radical (OH) by day or the nitrate radical (NO_3) at night. The condensing organics may be first, second or higher generation oxidation products. There is much debate about the dominant parent VOCs, though it is thought that biogenically produced compounds are particularly efficient producers of SOA. Such species may include fast-reacting monoterpenes and sesquiterpenes. There is also conflicting evidence about the effectiveness of isoprene as a potential SOA precursor.

Scientific activities

The Atmospheric Sciences Group of the University of Manchester has participated in a large number of field experiments investigating the physical and chemical properties of atmospheric aerosol in a variety of environments on both fixed ground-based and moving platforms. The range of instrumentation deployed allows the sizing and counting of aerosol particles from 3 nm to upwards of 10 μm diameter (by mobility, aerodynamic and optical instrumentation), the characterisation of the ability of the particles to take up water in the sub- and supersaturated environment and the determination of the composition of the non-refractory aerosol components by Aerosol Mass Spectrometer (AMS) measurements. The Group is also involved in a number of aerosol modelling activities, ranging from detailed multicomponent thermodynamic codes, organic partitioning predictions and regional particulate modelling. This brief report focuses on recent ground-based and aircraft measurements with particular emphasis on the organic aerosol fraction, presents evidence for a dominant contribution from SOA. It further poses some challenges associated with the mechanistic understanding of SOA formation.

Scientific results and highlights

Measurements made by AMS in a wide number of locations always show a significant contribution from organic components. There is an apparent global ubiquity of the larger size "accumulation" mode, with a similar characteristic fragmentation pattern associated with high oxygen to carbon ratio, the so-called oxygenated organic aerosol (OOA). In experiments conducted closer to pollution centres, a second, finer organic mode is observed. This mode has a characteristic fragmentation pattern with significant contribution from carbon chain fragments and a low oxygen content; the "hydrocarbon-like" organic aerosol (HOA). This is illustrated in Figure 1.

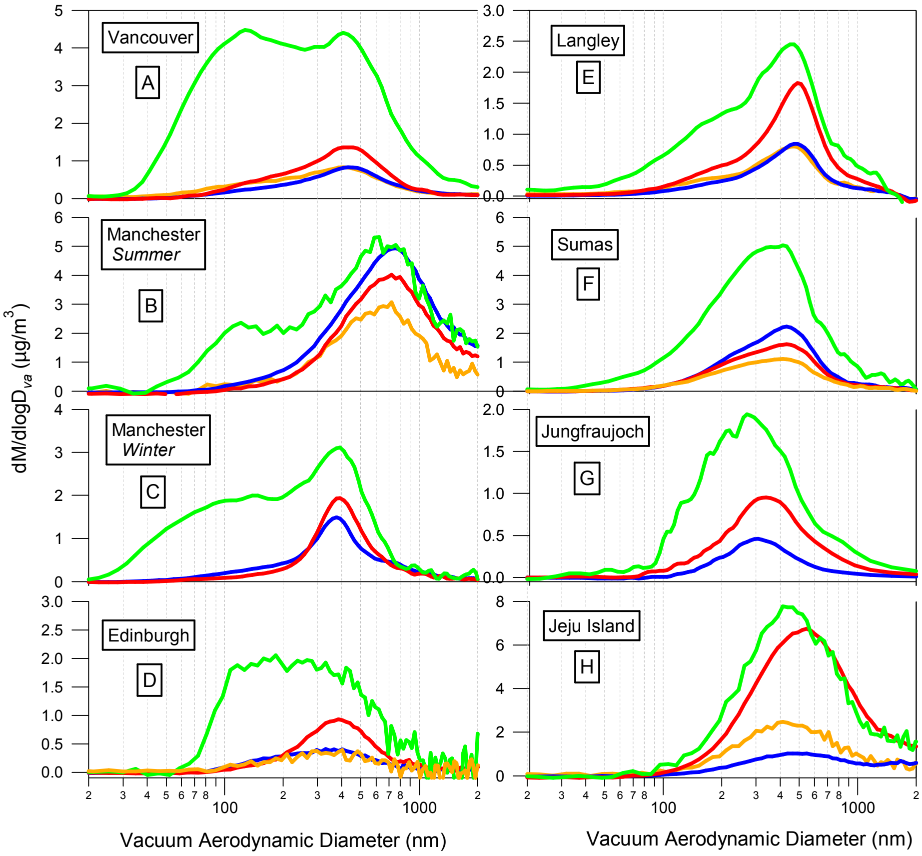
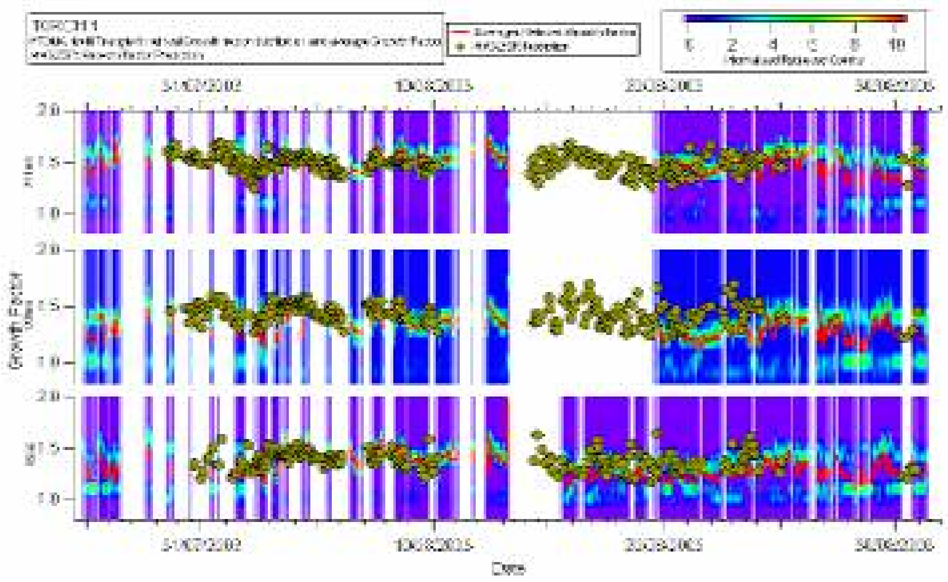


Figure 1. Average AMS component mass distributions from 6 National, EU, US and Korean collaborations [Allan *et al,* 2003; Alfarra *et al.*, 2004; Topping *et al.*, 2004]. The contributions from sulphate are shown in red, nitrate in blue, ammonium in orange and organic in green.

AMS component distributions, along with impactor measurements, have been used to initialise a detailed thermodynamic model, ADDEM [Topping *et al.,* 2005a, 2005b] and a simpler additive representation to predict water content of aerosol particles for comparison with direct measurements of hygroscopic growth using a hygroscopic tandem differential particle analyser (HTDMA) in two field experiments within the Tropospheric ORganic CHemistry (TORCH) project aimed at specific characterisation of organic species partitioning. In all cases, reasonable closure is obtained with a modest growth factor of the organic component of around 1.1 to 1.2 at 90 % RH [McFiggans *et al.*, 2005; Gysel *et al.*, 2006; Corris *et al.*, in prep).



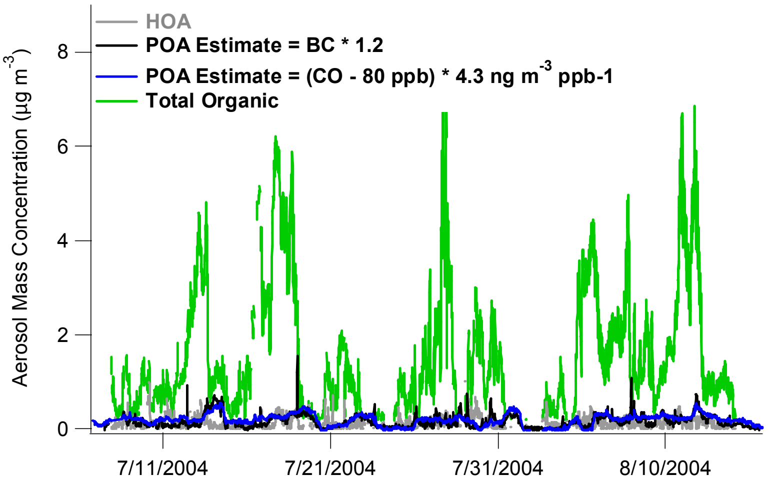


Figure 2. Predicted $GF_{D,90\%}$ (growth factor at 90% RH) using AMS measured mass of each component, compared with HTDMA $GF_{D,90\%}$ measured through the TORCH 2003 experiment in Writtle, 30 km North East of London.

AMS measurements in polluted background air show that the HOA fraction makes up only a small fraction of the total OA burden (and one which is scaleable to primary anthropogenic pollutants such as black carbon and carbon monoxide). This provides indirect evidence that the HOA may have a similar signature to the primary organic aerosol (POA) component. Figure 3 shows the relative contribution to the total aerosol burden from HOA compared with POA estimates scaled to BC and CO from measurements made in Nova Scotia in US outflow conditions.

Measurements made from the UK Facilities for Airborne Atmospheric Measurements (FAAM) BAe 146 aircraft have revealed further evidence for a large contribution from non-primary OA from a number of field projects.

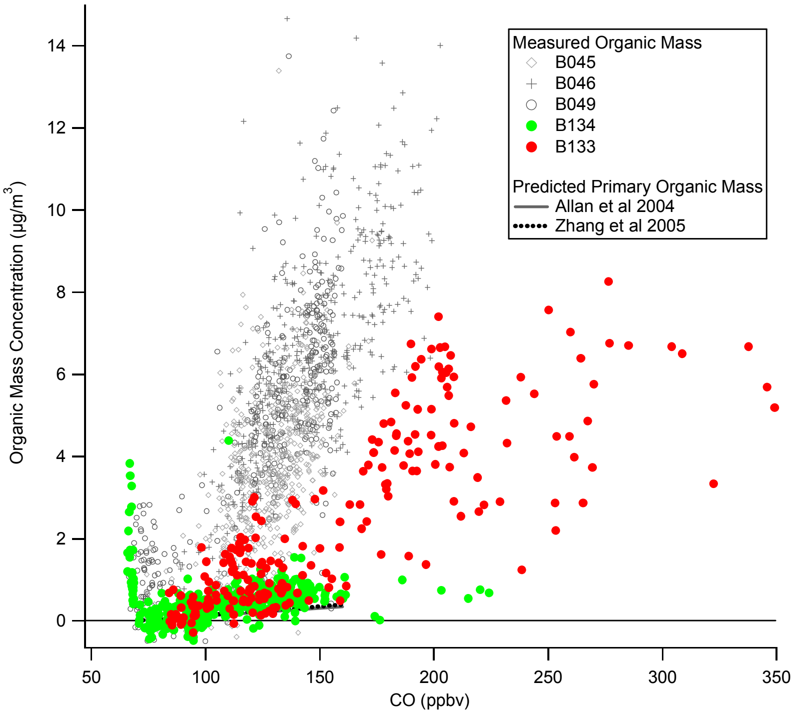


Figure 4. Measurements of organic mass from the ADRIEX project in the Po Valley (grey symbols), an advective flight (green symbols) and a more stagnant flight (red symbols) from the AMPEP project around the UK plotted against the measured CO concentration and two predictions of POA. In all cases, there is a requirement for a significant secondary contribution

Along with recent work of DeGouw *et al.* [2005], McFiggans *et al.* [2005] and Cubison *et al.* [2006] suggesting that the AMS measured OOA contribution increases with photochemical age and that of Volkamer *et al.* [2006] and ongoing work of Zhang *et al.* (in preparation) further suggesting that the OOA is synonymous with SOA, these studies show that SOA consistently makes up a large fraction of the aerosol burden.

It is therefore necessary to carry a meaningful description of SOA production in models aiming to reproduce aerosol processes on any scale. The Model of Aerosol Dissolution, Reaction, Ionisation and Deposition (MADRID) version of the US EPA Community Multiscale Air Quality (CMAQ) model, frequently referred to as Models-3, has been used for 3-way nested simulations centred on the UK. MADRID has been specifically designed to realistically represent aerosol processes and carries a sectional representation of aerosol dynamics and a detailed parameterisation of mass transfer of condensing inorganic and organic species to the evolving size distribution. In the version of MADRID used, SOA formation is represented by an extension to the RADM2 chemical scheme and considers the oxidation of 2 lumped anthropogenic SOA parent molecules and 12 potential biogenic parent species to produce condensable organic precursors. The “condensability” of the precursors is represented by partitioning coefficients derived from 2 or 4-product fits to chamber data, assuming absorptive partitioning to an organic phase. Figure 5 illustrates that the predicted SOA loading from the two lumped anthropogenic precursors makes an almost negligible contribution to organic aerosol averaged across the entire UK domain. The biogenic contribution using the scheme is still under investigation, but may be expected to provide a greater mass than the anthropogenic sources.

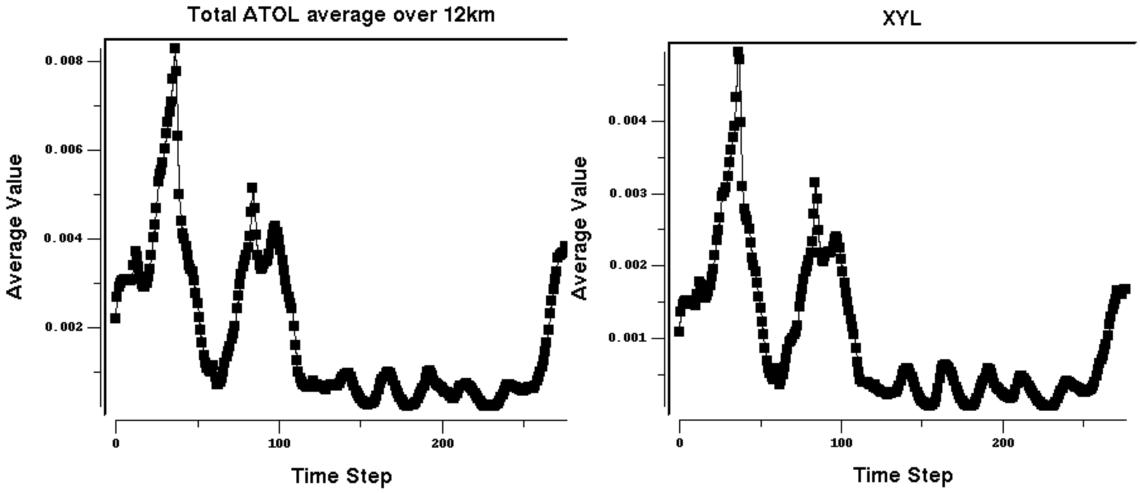


Figure 5. Average domain mass loadings from the two anthropogenic aerosol components ATOL (from all species less reactive than toluene) and AXYL (from all species more reactive than xylene). The peak loadings at less than 0.01 and 0.005 μgm^{-3} respectively, make a negligible contribution to aerosol loading.

It might be expected that such schemes will not realistically represent organic aerosol production owing to the mechanistic assumptions employed and the source of the data used in the mechanism. To address the latter point, it can be seen from Figure 6 that chamber experiments carried out at unrealistically high precursor concentrations produce aerosol of a composition less like that in the atmosphere than those carried out at low precursor concentration.

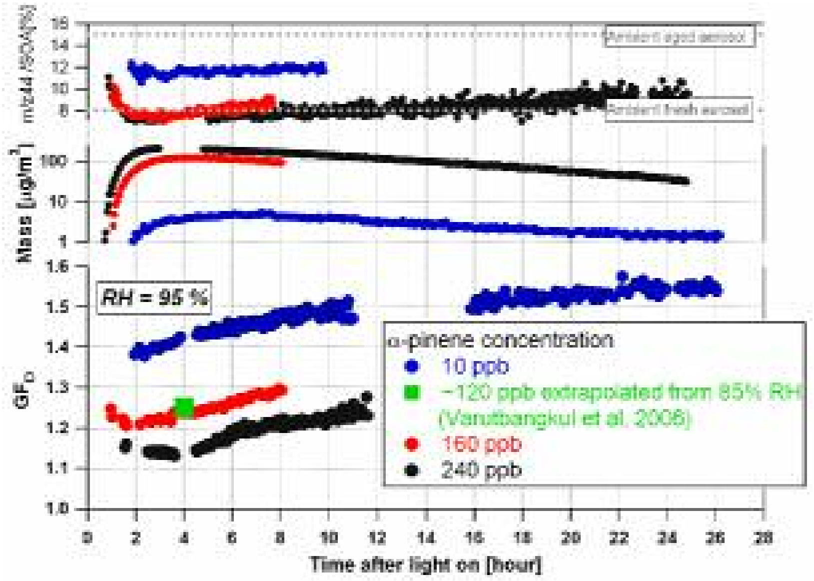


Figure 6. Results from chamber formation of SOA from different concentrations of α-pinene. The top panel shows that the AMS fragmentation pattern more closely resembles that of atmospheric SOA when low concentrations are used and the bottom panel that the hygroscopic growth factor is dependent on the aerosol composition. Both the chemical composition and physical properties are therefore dependent on realistic chamber conditions.

The first point, however, may be even more important. Since aerosol particles are formed in the moist atmosphere, they will likely contain significant water and condensation of organic material will proceed to a wet aerosol. In addition, any particle is likely to contain inorganic material and organic components will be at a lower concentration than in particles freshly nucleated from organic vapours (altering the rates of any concentration-dependent condensed phase reactions). Mechanisms of SOA formation should reflect this fact.

Future outlook

It is evident from atmospheric measurements that it is important to capture SOA formation and its contribution to the OA burden accurately. It is also evident that assumptions surrounding available mechanistic treatments may limit our ability to make useful predictions. Since the organic aerosol component is likely to be very complex, a technique suitable for large scale models must contain a useful protocol for lumping the precursors and aerosol components. Figure 7 illustrates a methodology for lumping the condensable species according to the properties which will dominate SOA formation and OA behaviour once formed. Data available for such a lumping are sparse, but the best available data may be incorporated into the framework flexibly. Such data may be forthcoming from chamber experiments under appropriate conditions and from existing predictive techniques. However, care must be taken when predicting such properties; particularly the vapour pressures of multifunctional compounds. It is the intention to incorporate such a scheme (with the associated thermodynamic simplifications) into a predictive framework to capture OA on a number of scales.

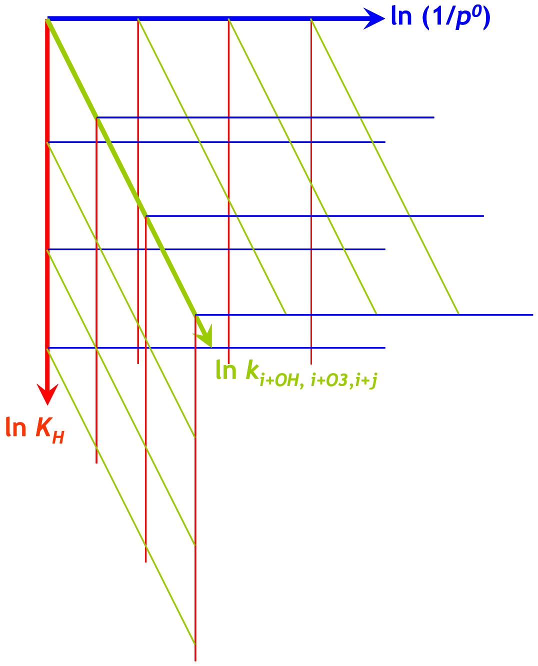


Figure 7. A framework to account for all possible SOA formation routes must include the vapour pressure of all components, the ability of the components to partition to an aqueous medium and the reactivity of the components once condensed. Validated predictive techniques and laboratory data for lumping of components are sparse at present and will be the focus of future research

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Potential of Isoprene to Contribute to Secondary Organic Aerosol Formation

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Summary

In the current study the potential of Isoprene to contribute to secondary organic aerosol (SOA) formation and the SOA chemical composition is investigated in a series of laboratory chamber experiments. SOA yields from photooxidation of isoprene agree fairly well with previous data. SOA properties and composition is studied using matrix-assisted laser desorption mass spectrometry and online aerosol mass spectrometry. The formation of high molecular weight compounds over the course of 15 hour experiments is shown which is attributed to oligomerization reactions occurring in the aerosol phase. Real time particle mass spectra colleted continuously by an Aerodyne Aerosol Mass Spectrometer imply a higher contribution of more carbonyl containing compounds and monoacids relative to multifunctional acids. With increasing age of the aerosol higher mass fragments appear and the aerosol gets more oxidized.

Introduction

Recently special attention has been paid to the secondary organic aerosol (SOA) formation from the photooxidation of Isoprene. Observations of proposed isoprene oxidation products in ambient $PM_{2.5}$ [Claeys, 2004; Edney, 2005] and laboratory heterogeneous reaction systems [Kalberer, 2004; Surratt, 2006; Jang, 2002; Limbeck, 2003; Kroll, 2006; Kroll, 2005] suggest that isoprene might play an important role in SOA formation due to its large source strength globally [Guenther, 1995]. In order to better understand the chemical mechanism of aerosol growth by the photooxidation of isoprene an extensive characterization of the system was done.

Scientific activities

Photooxidation experiments were carried out in a 27 m^3 Teflon chamber. Experimental protocols are previously described [Dommen, 2006; Paulsen, 2005]. A suit of different experimental techniques is used to investigate gas phase chemistry and aerosol properties: proton-transfer-reaction mass spectrometry (PTR-MS), Volatility Tandem Differential Mobility Analyzer (VTDMA), Matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS) and Aerodyne Aerosol Mass Spectrometer [Dommen, 2006].

Scientific results and highlights

We measured SOA yields from isoprene photooxidation in the PSI smog chamber to be higher than previously reported and also observed SOA formation at lower initial concentrations. Nevertheless, mass yields were still low at 0.2-5 % for 200 – 2000 ppb of isoprene [Dommen, 2006]. In general a good agreement between different studies was found except for experiments with H_2O_2 as radical source (Figure 1). In contrary to the work of [Kroll, 2005; Kroll, 2006; Surratt, 2006] no aerosol formation was observed below 250 ppb of Isoprene.

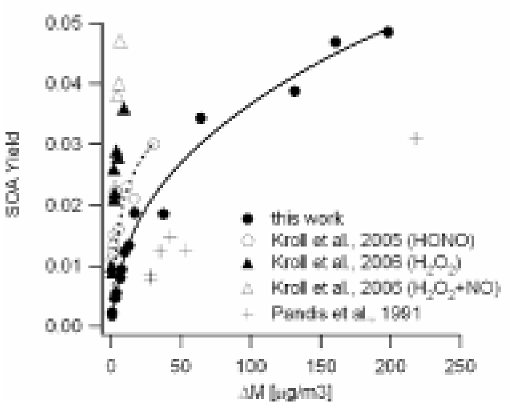

Figure 1. Measured SOA yields from the isoprene photooxidation in the PSI smog chamber compared to literature data

Results from laser desorption ionization mass spectrometry and volatility tandem differential mobility analyzer measurements suggest that also for the isoprene system oligomerization reactions occur within the aerosol. Figure 2, left panel, shows MALDI-MS spectra of isoprene SOA collected between 1.6-2.8 and 14.0-16.0 hours after start of irradiation. Already after 2 hours high mass peaks are observed. These grow with time in intensity and still higher mass peaks start to appear. After 15 hours a regular pattern between m/z 100 and 600 with mass differences of 14, 16 or 18 is observed, typical of a polymeric substance. The formation of oligomers was further supported by volatility measurements [Dommen, 2006].

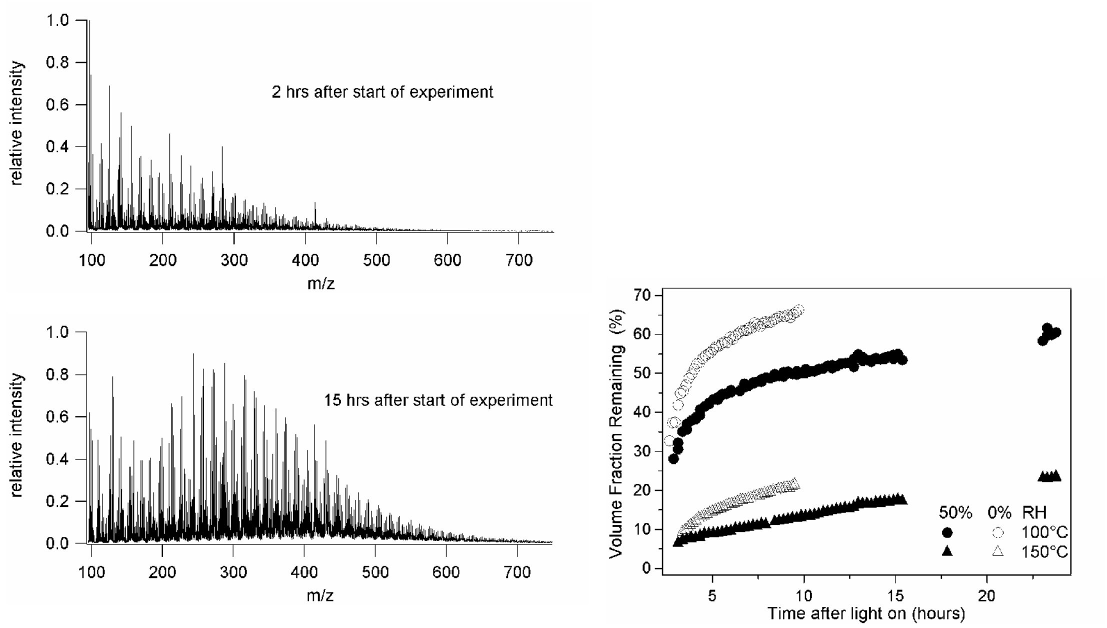

Figure 2. Left panel: Matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS): Mass spectra of aerosol from isoprene photooxidation collected on steel plates in an impactor after 2, 6 and 15 hours of irradiation. Initial isoprene mixing ratio was 2.5 ppm and nucleation started after 65 min. High molecular weight molecules appear, which can be interpreted as oligomers. Right panel: Volatility of isoprene aerosol at different temperatures and RH. A continuous increase of the volume fraction remaining can be observed which indicates that SOA becomes less volatile with time.

Figure 2, right panel, presents the volume fraction remaining (VFR) of the aerosol at 100 and 150 °C and at0 and 50 % RH. The continuous increase of the VFR over 25 hours indicates that the aerosol becomes less volatile over time. At 100°C a fast increase of the VFR from 27 to 44 % occurs over the first 5 hours and then steadily increases to 62 %. At 150°C a steady increase from 5 to 25 % is measured. This decrease of volatility can be caused both by oxidation of the species and by reactions in the aerosol phase like addition or condensation of two compounds forming a higher molecular weight species. The MALDI-MS result favours the latter explanation [Dommen, 2006].

Real time particle mass spectra were colleted continuously by an Aerodyne Aerosol Mass Spectrometer. Mass spectra and their logarithmic representation averaged for one hour after 4 and 8 hours of irradiation are shown in Figure 3. All spectra are normalized to the sum of total of all mass fragments, providing a quantitative fractional contribution of each mass fragments to the total measured mass. Spectra show a higher contribution of m/z 43 compared to m/z 44 which implies more carbonyl containing compounds and monoacids relative to multifunctional acids (Figures 3A and 3B). With increasing age of the aerosol higher mass fragments appear (after 8 hours) (Figures 3C and 3D).

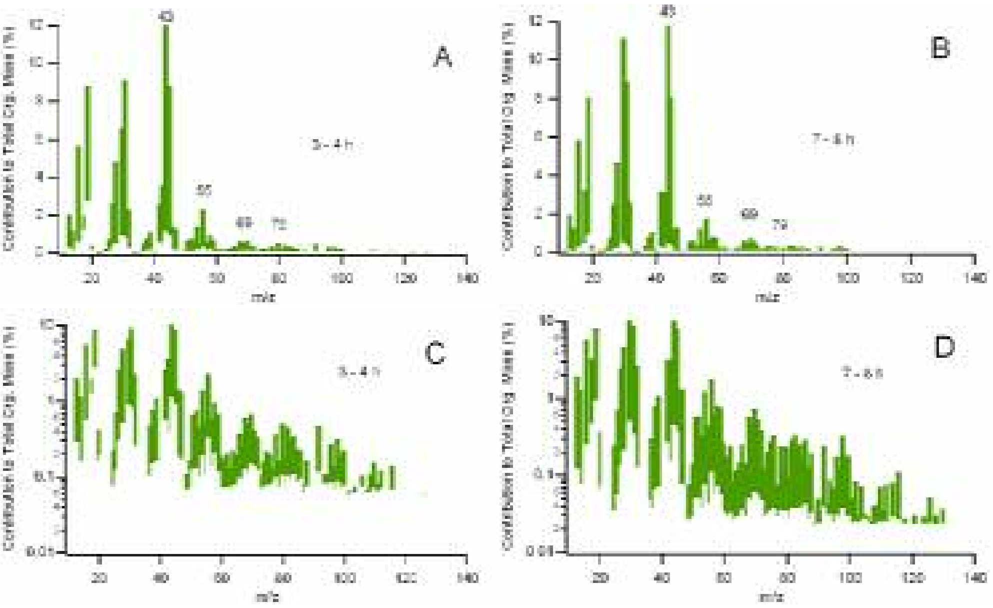

Figure 3. (A and B) Mass spectra averaged for one hour after 4 and 8 hours of irradiation. All spectra are normalized to the sum of total of all mass fragments, providing a quantitative fractional contribution of each mass fragments to the total measured mass. The white bars at the bottom of individual mass fragments are the associated errors. (C and D) Logarithmic presentation of the mass spectra shown, in order to illustrate better the distribution patterns of low intensity mass fragments. The white bars at the bottom of individual mass fragments are the associated errors.

In Figure 4 the percentage change in the fractional contribution to total mass of individual mass fragments at 8 hours compared to that observed at 4 hours of irradiation. A delta value (Δ = m/z-14 n + 1, where n is the nominal number of CH_2 groups left on the functional group) is calculated for each m/z, which is an indication of the functionality of the fragment. For example, $D < 0$ are associated with unsaturated and aromatic compounds while $D > 2$ are indicative for oxygenated organics [Bahreini, 2005]. Delta values are indicated with colors. It appears that the decreasing fragments have more negative delta values. SOA appears to be more oxidized with time.

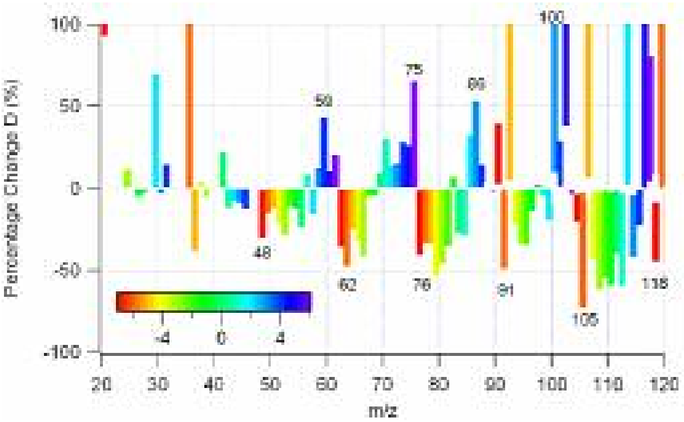

Figure 4. The percentage change in the fractional contribution to total mass of individual mass fragments at 8 hours compared to that observed at 4 hours of irradiation. A delta value (Δ=m/z-14n+1, where n is the nominal number of CH_2 groups left on the functional group) is calculated for each m/z, which is an indication of the functionality of the fragment. For example, $D < 0$ are associated with unsaturated and aromatic compounds while $D > 2$ are indicative for oxygenated organics. Delta values are indicated with colors. The white bars at the bottom of individual mass fragments are errors propagated through the calculation.

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On the Importance of Isoprene as a Secondary Organic Aerosol Precursor

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Motivation

Atmospheric particles are known to affect health, visibility and climate and act as substrates for heterogeneous reactions in the atmosphere. Organics, in particular secondary organic aerosols (SOA), are an important component of tropospheric particles. Although SOA can not be directly measured, there is strong computational and observational evidence that SOA is a major contributor to organic aerosol mass in the atmosphere [Tsigaridis *et al.*, 2006; Volkamer *et al.*, 2006]. Modelling studies provide a wide range of global SOA burden [Kanakidou *et al.*, 2005]. The evaluation of SOA computations by comparison with field measurements shows important discrepancies both in the free troposphere [Heald *et al.*, 2005] and the boundary layer [Volkamer *et al.*, 2006]. Since models rely on knowledge acquired from chamber experiments, this discrepancy could be due to: i) inadequacy of the chamber experiments for atmospheric conditions, ii) missing gas phase precursors, iii) missing pathways of SOA production from the already considered precursor molecules.

Recent field and chamber experiments prove that isoprene can be a precursor of organic aerosol in forested areas [Clayes *et al.*, 2004; Kroll *et al.*, 2005] and suggest that it also can affect the CCN composition in remote marine regions [Meskhidze and Nenes, 2006]. Note that isoprene is the second most abundantly emitted hydrocarbon in the atmosphere after methane (500 Tg/yr; Guenther *et al.* [1995]). In addition, SOA can be also formed through cloud processing, with glyoxal (CHOCHO) being a key compound in this SOA production pathway [Lim *et al.*, 2005; Warneck *et al.*, 2005].

The present study focuses on the global production of Secondary Organic Aerosols (SOA) from isoprene oxidation followed by gas-to particle conversion and on the involvement of glyoxal on tropospheric chemistry.

Simulations and discussion

For this study the 3-dimensional global chemistry transport model v.4 (TM4), a coupled aerosol [Tsigaridis *et al.*, 2006] and gas-phase chemistry [Poisson *et al.*, 2000] transport model of the troposphere and lower stratosphere [Wittrock *et al.*, 2006] has been used.

The two-product model [Odum *et al.*, 1997; Henze and Seinfeld, 2006] has been adopted to describe the global production of SOA from isoprene based on the parameters given from Henze and Seinfeld [2006]. According to our calculations on an annual mean basis, the inclusion of isoprene as a precursor of SOA is increasing regionally both the boundary layer and the free troposphere secondary organic aerosol mass by more than 40 %, respectively (Figure 1). However, this increase does not appear to be sufficient to account for the discrepancy between model results and observations. On a global scale isoprene increases by 60 % the global chemical production of SOA from biogenic hydrocarbons that in our simulation is estimated at 30 Tg/yr. The overall isoprene impact on SOA production is due to i) direct production of SOA from isoprene and ii) further enhancement of SOA produced by other parent hydrocarbons due to the availability of SOA from isoprene for gas-to particle partitioning. The estimated isoprene contribution to SOA is higher than the 40 % estimated by Henze and Seinfeld [2006], who used the same two product model parameters but a different chemistry transport model.

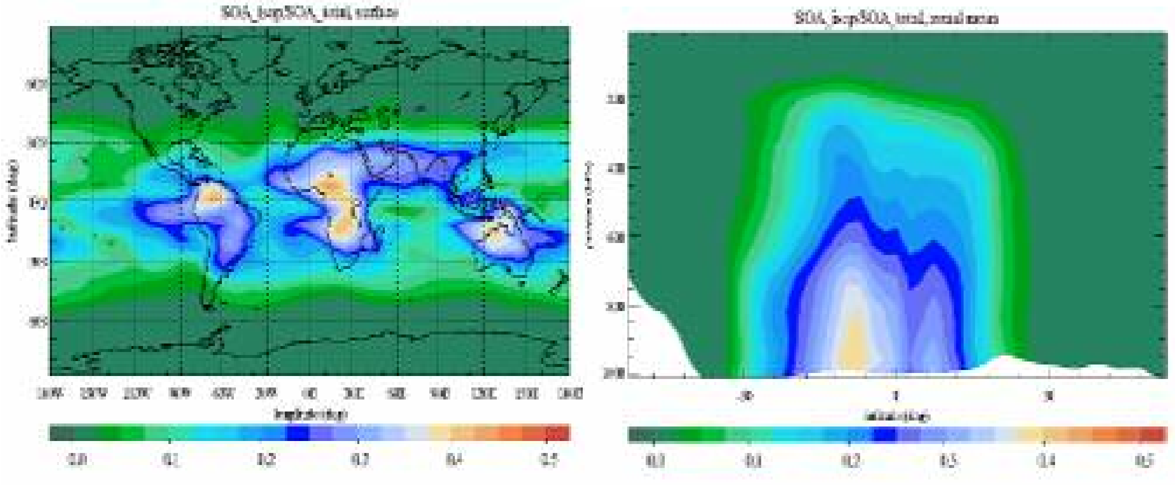

Figure 1. Simulated ratio of SOA produced from isoprene oxidation to the SOA from all precursors, annual mean values for surface (left panel) and zonal mean (right panel).

Glyoxal is the smallest α-dicarbonyl formed from the oxidation of numerous VOCs [Carvert *et al.*, 2000; Volkamer *et al.*, 2005]. The involvement of glyoxal in cloud processing may contribute 1.6 Tg yr^{-1} in global SOA production [Lim *et al.*, 2005]. In the TM4 chemical scheme, glyoxal is produced mainly from biogenic hydrocarbons (70 %) but also from acetylene (15 %) and anthropogenic aromatic hydrocarbons (10 %). TM4 is able to simulate the global concentrations of glyoxal as observed by the SCHIAMACHY [Wittrock *et al.*, 2006]. The most recent TM4 glyoxal simulations with the updated chemical scheme with regard to glyoxal production based on Volkamer *et al.* [2005] kinetic experiments are presented in Figure 2. These distributions show the observed tropical hot spots as well as the smaller enhancement of glyoxal over polluted areas in the northern hemisphere.

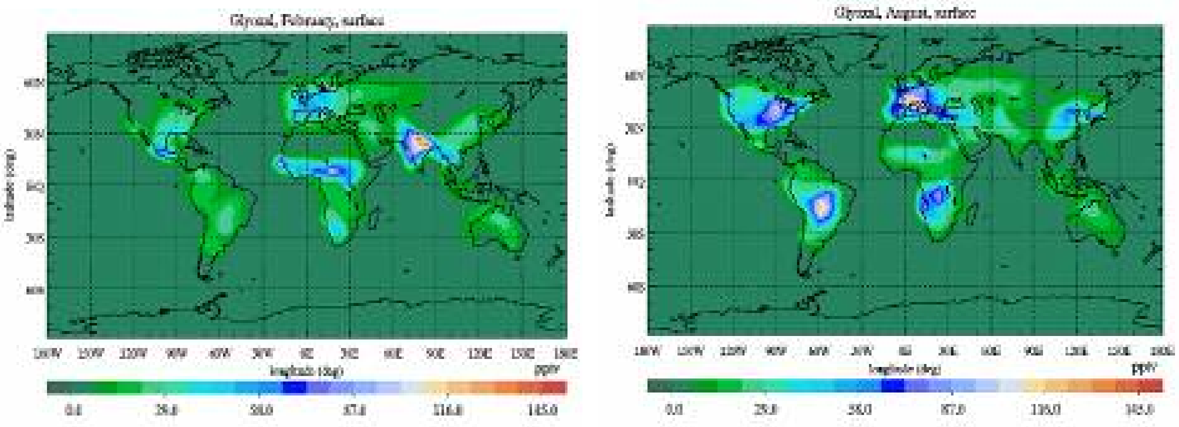

Figure 2. Glyoxal surface distribution in February (left panel) and in August (right panel) in pptv as simulated by TM4.

Further developments

Our TM4 model simulations show the potential importance of isoprene as a precursor of SOA on global scale. The contribution of these simulations in reducing the discrepancy between model results and observations remains to be determined together with the importance of aqueous phase chemistry and the involvement of glyoxal in producing SOA in the troposphere.

Acknowledgements

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Measurement of Organic Aerosol Precursors over an Oak Forest

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 1

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Summary

Emission fluxes of isoprene, its oxidation products, and other oxygenated VOCs were measured using eddy covariance above a mixed oak forest in southern England during summer 2005. VOC concentrations were measured using proton-transfer reaction mass spectrometry. Fluxes of isoprene and its oxidation products (MVK and MACR) followed a diurnal pattern consistent with biogenic emission from the forest canopy. Fluxes of other oxygenated VOCs followed a more complex pattern, consistent with vehicle-related sources beyond the forest.

Introduction

Emissions of biogenic VOCs from forests can be estimated from leaf/branch measurements made using cuvettes, scaled by the use of models to encompass the range of light and temperature regimes present in a forest canopy. This combined measurement and modelling approach necessarily has to be used for estimating emissions on regional, national and global scales because of the impossibility of making field measurements of VOC fluxes across the variability represented by the earth's forests. However, it is important that such model estimates be reconciled with actual field measurements at some sites, to ensure that the model estimates reproduce the true pattern of emissions in response to a changing environment. Moreover, it is important to be sure that the models include all the relevant sources (*e.g.* leaf litter or under-storey vegetation). Direct field measurement of VOC fluxes above a forest has become possible through the development of fast-response (> 1 Hz) sensors that can be used with sonic anemometry to measure fluxes using the methods of eddy covariance. This contribution reports initial flux data from measurements made above an English oak forest using Proton-Transfer Reaction Mass Spectrometry (PTR-MS) for the rapid quantification of VOC concentrations, coupled with sonic anemometry. In this study, simultaneous fluxes of ozone and aerosols were made, but only the VOC data are reported here.

Scientific activities

The measurement site was at Alice Holt, Straits Enclosure, Hampshire (51^o 7' N; 0^o 51' W), a managed lowland mature oak forest (*Q. robur* and *Q. petraea*) interspersed with ~ 10 % ash (*Fraxinus excelsior*). Measurements were made during July and August 2005. Sensible heat and momentum fluxes were measured using a Gill Solent R1012A ultrasonic anemometer; VOC concentrations were measured using an Ionicon Proton Transfer Reaction Mass Spectrometer (PTR-MS). Other measurements included aerosol components (Aerodyne Aerosol Mass Spectrometer), total particle number (5-2000 nm diameter) (Condensation Particle Counter) and ozone (modified fast response GFAS sensor; [Gusten and Heinrich, 1996]).

Air for PTR-MS analysis was sampled down a 30 m Teflon tube mounted on top of a 25 m tower, from immediately below the sonic anemometer (fig 1). Standard drift tube conditions were used (E/N = 120 Td), and a daily instrument background was measured using a Pt/Al_2O_3 catalyst heated to 200 ^{o}C. Two measurement modes were used:

1. Scanning a range of masses (m/z 21 – 141) at 0.5 s/scan; scans were made at 0 and 30 minutes past the hour for 5 min;
2. 8 or 9 predefined masses (m/z) were scanned for 25 min, including m/z 21, 33, 37, 41, 45, 47, 59, 61, 69 and 71. (20 ms on m/z 21 and 37, and 50 ms on all other masses). Note that masses represent m/z for the protonated analyte (MW+1).

Concentrations were calculated using reaction rate constant (k) values from Zhao and Zhang [2004] and reaction time (t) values were calculated from $t = L/vd$ [Lindinger, 1998]. Fluxes were calculated using a 2 s lag time.

Figure 1. Measurement site in Alice Holt forest, showing the access tower and (inset) the PTR-MS inlet immediately below the sonic anemometer.

Scientific results and highlights

Major emissions were isoprene, methyl vinyl ketone and methacrolein (MVK+MACR, which are not separated by PTR-MS), acetaldehyde, acetic acid, acetone and methanol. Median concentrations (20th July 2005 to 18th August 2005) were 0.10 ppb, 0.01 ppb, 0.26 ppb, 0.02 ppb, 0.38 ppb and 1.50 ppb respectively. Emissions correlated well with temperature (Figure 2).

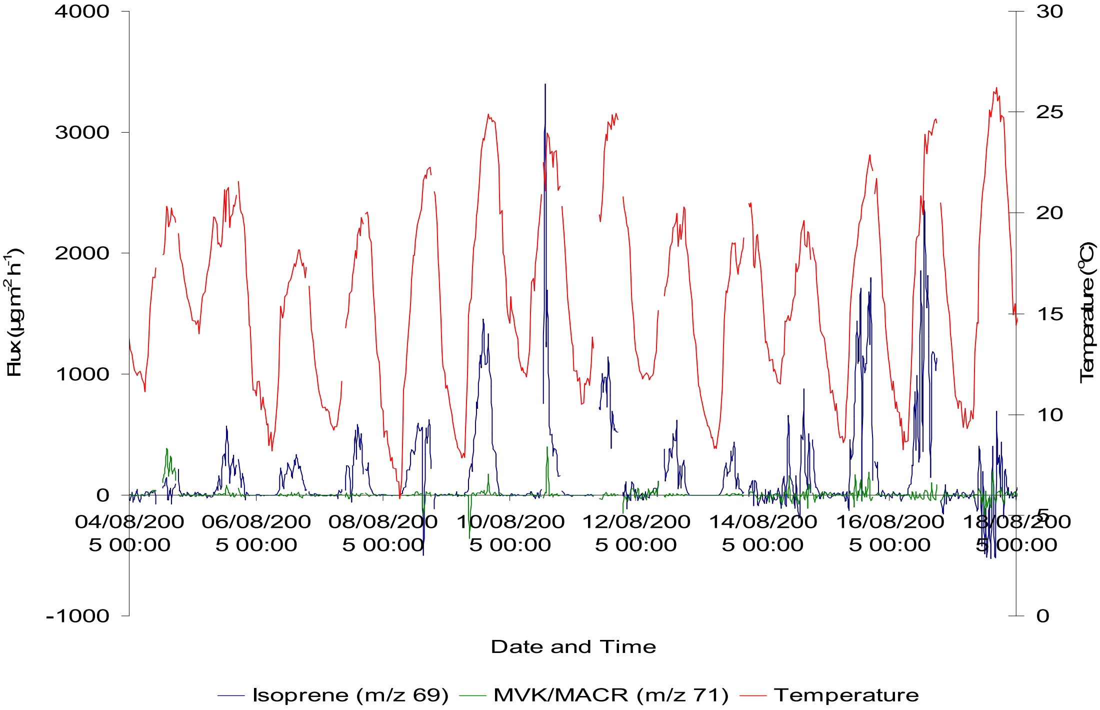

Figure 2. Isoprene and MVK/MACR flux and temperature variation, 4th August to 18th August 2005.

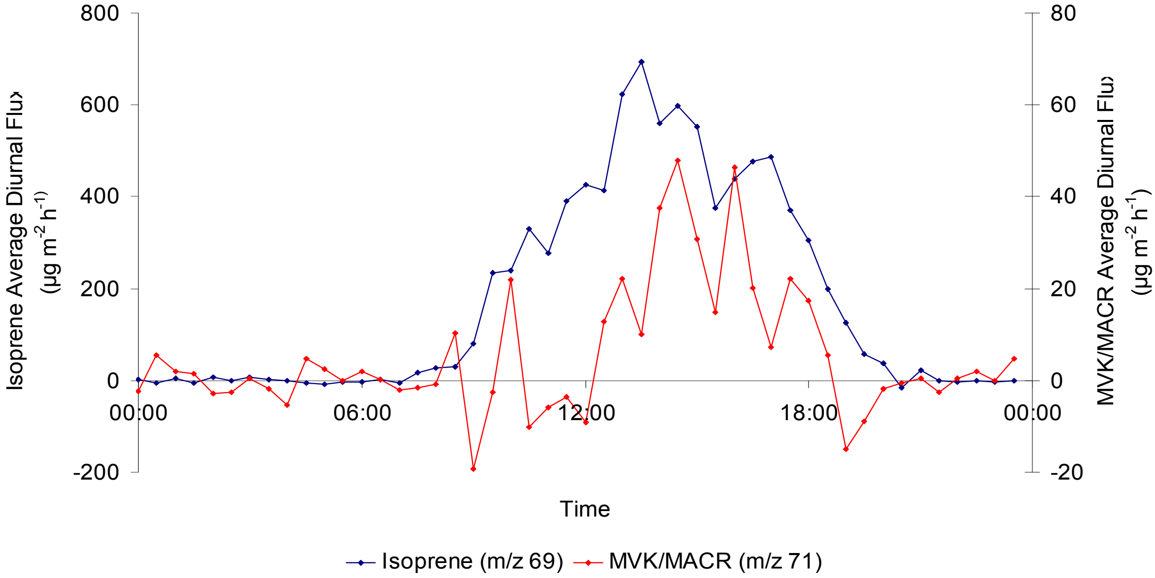

Figure 3. Average diurnal flux of isoprene and MVK/MACR, 4th August to 18th August 2005.

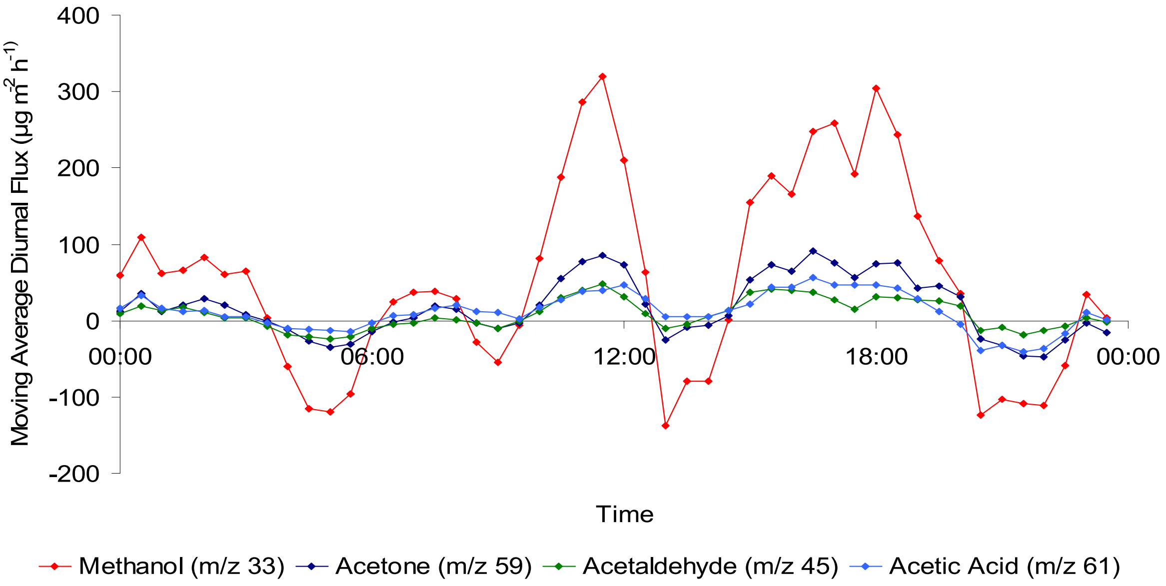

Figure 4. VOC average diurnal flux from 4th August to 18th August 2005. Probable contribution from a nearby main road.

Clear diurnal trends of all VOCs were seen (Figures 3 and 4). Although the fluxes of isoprene and its oxidation products usually followed the expected diurnal pattern, peaking in early afternoon (Figure 3), other VOC fluxes had a more complex pattern, suggesting a role for anthropogenic emissions from local road traffic (Figure 4).

Future outlook

The results presented here are being analysed for comparison with the simultaneous fluxes of ozone and particles made by colleagues, and for a more detailed analysis of some of the signals, *e.g.* the contribution of isoprene fragments to m/z 41. An automated diffusion calibration system is being developed for a range of VOCs to permit field calibration of the PTR-MS, and a system for parallel GC-FID analysis using pre-concentration and thermal desorption has been constructed, to facilitate the assignment of individual m/z values to specific VOCs.

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Towards Modelling SOA with LOTOS-EUROS

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Summary

We are working on the incorporation of secondary organic aerosols (SOA) in our modelling system LOTOS-EUROS. For this purpose we have updated the biogenic emissions of mono-terpenes based on Simpson *et al.* [1999] in combination with an European tree-species database. Further, we have introduced a SOA formation mechanism in the model. Below the first results are shown.

Introduction

Carbonaceous aerosol comprises a mayor part of the total aerosol mass. Hence, they are of special interest for the climate community as they exert a significant climate forcing. Furthermore, they are suspected to contribute to the occurrence of adverse health effects (as a consequence of inhaling particles/PM). However, chemistry transport models are not able to reproduce ambient EC and OC levels, which is needed to become more confident in our understanding of the causal relations between activities/emisisons and particle concentrations in the atmosphere. The LOTOS-EUROS model under-estimates OC by about a factor 2. The gap may be explained by too low primary emissions but may also be partly explained by SOA formation which has not been included in the model up to now. Here we report on the first efforts to include SOA formation in LOTOS-EUROS.

Scientific activities

Land-use data

The starting point in this study was the official Corine/Phare Land Cover Data from the EEA, which was completed for the full European domain by Smiatek (FI-Garmisch Partenkirchen) using (mainly) the Pelinda data base. The Corine/Smiatek data base has been enhanced using the tree species map for Europe made by Koeble and Seufert [2001], who also used Corine as a basis. This data base contains 115 tree species, on a grid of 1 × 1 km^2, with coverage per grid. In parts of the area, especially Russia, the Koeble tree map gives no information. We started with Corine/Smiatek land use database, and filled this in with the tree data, when the tree database has no information; the three Corine forest categories are maintained. So, the full tree data base contains 115 + 3 categories. The database has a resolution of 0.0166 × 0.0166 degrees which is aggregated to the required resolution during the start-up of a model simulation.

Model development

The LOTOS-EUROS model [Schaap *et al.*, 2006] was extended with a module to calculate the terpene emissions from forests following Simpson *et al.* [1995; 1999]. The emissions are a function of tree species, biomass density, light intensity and temperature.

The CBM-IV chemical mechanism of the model was extended for inclusion of the CMU/STI SOA formation module following Pun *et al.* [2003]. This module accounts for the formation of 6 condensable gases from selected gas phase reactions. Two of these components derive from terpenes.

Scientific results and highlights

We have calculated the terpene emissions for a full year, *i.e.* 2001. The emission distribution is given in Figure 1. The total emission in the area shown is 4.8 Tg. Compared to Simpson *et al.* (1999) this value is slightly higher, which can be attributed to a combination of the slightly larger domain in this study, different tree distributions and other meteorological conditions.

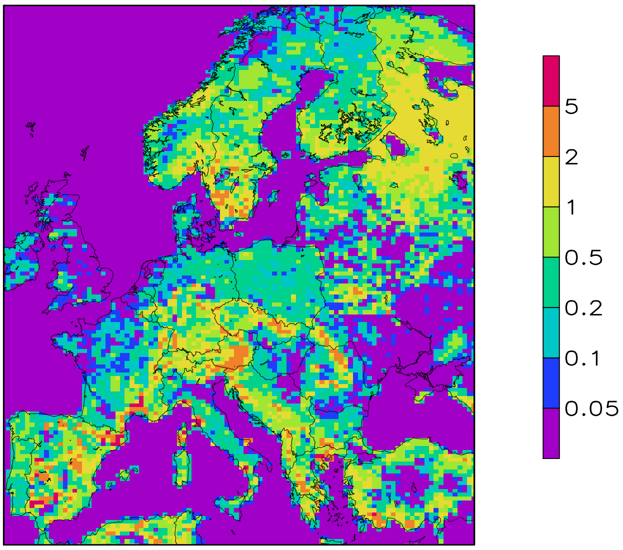

Figure 1. Emission distribution (Gg/cell) of mono-terpenes derived in this study

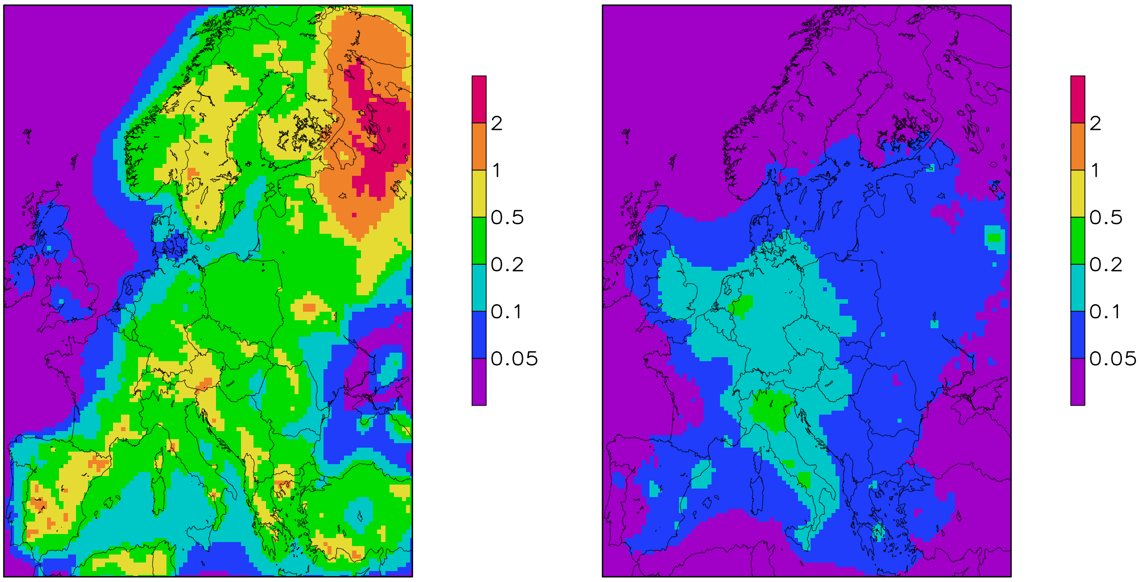

Figure 2. First model results for biogenic SOA (left) and anthropogenic SOA concentrations (µg/m^3) for July, 2001.

The model results indicate that biogenic SOA clearly dominates the SOA burden over Europe. This finding is well known from many earlier studies. However, the uncertainties in the shown distributions are large. First of all, SOA modelling in general is associated with a large uncertainty. Moreover, these results are the first with this system and some parts of the cycle (wet and dry deposition) for SOA and especially its precursors still need to be updated. Improvements of the schemes in the model are expected.

Future outlook

We will further develop the relevant parameterizations for SOA formation and removal in the model. Also, a new emission inventory on carbonaceous (EC/OC) particles is expected soon. Attention will be given to the representation of primary OC as a semi-volatile component. The system will be used to perform simulations for 2002-2003 to investigate if we can reproduce spatial and temporal patterns of carbonaceous aerosol over Europe.

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How Important is Secondary Organic Aerosol (SOA) for the Total Aerosol Optical Depth in the Troposphere?

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Motivation and approach

To elucidate the contribution of secondary organic aerosol (SOA) to the aerosol optical depth in the atmosphere, a coupled aerosol and gas-phase chemistry transport model of the troposphere and lower stratosphere has been used [Tsigaridis *et al.,* 2006]. The 3-d model focused on the aerosol chemical composition change since preindustrial times considering the secondary organic aerosol formation together with all other main aerosol components including nitrate. In particular, the non-sea-salt sulfate (nss-$SO_4^=$), ammonium (NH_4^+), nitrate (NO_3^-), black carbon (BC), sea-salt, dust, primary and secondary organics (POA and SOA) have been evaluated with a focus on the importance of secondary organic aerosols. The model simulations are described in detail by Tsigaridis *et al.* [2006].

AOD calculations are based on wet aerosol mass concentrations, size resolved specific extinction coefficients for sea-salt are based on Shettle and Fenn [1979], for dust on Patterson [1981] and on Volz [1973], while for the rest of the aerosol components the specific extinction coefficients in $m^2g^{-1}$are 5 for $SO_4^=$ and NO_3^- [Jeuken *et al.,* 2001], 9 for BC [Liousse *et al.,* 1996; Tegen *et al.*, 1997] and 4 for POA and SOA [Liousse *et al.*, 1996]. Ammonium aerosol contribution is included to that of sulfate and nitrate. The specific extinction coefficients are corrected for the effect of relative humidity as explained in Tsigaridis *et al.* [2006]. This has to be viewed as the upper limit for the water effect on aerosols and AOD, since hydrophilic carbonaceous aerosols are expected to be less hydrophilic than sulfate [Kanakidou *et al.*, 2005]. The lower limit of this effect is calculated by the assumption that only sulfate and nitrate extinction coefficients are affected by water uptake. The resulting AOD is calculated to be 20 % lower than the base case where all hydrophilic aerosols are treated like sulfate, pointing out that the error introduced by that assumption is lower than 20 %.

Results and discussion

The global mean Aerosol Optical Depth (AOD) at 550 nm calculated by the model increased from 0.084 in the preindustrial atmosphere to 0.102 nowadays, a value smaller than the satellite measurements, mainly due to the underestimation of some aerosol components burden. On average, the model tends to underestimate the AERONET network observations by about 10 %. There is a general trend on underestimating the AOD measurements, with the exception of Africa, where a general overestimation is calculated. The overestimation in the AOD calculations over Africa, mostly attributed to dust load, can explain the high global annual mean percent contribution of dust to the AOD, for both the preindustrial and present atmospheres.

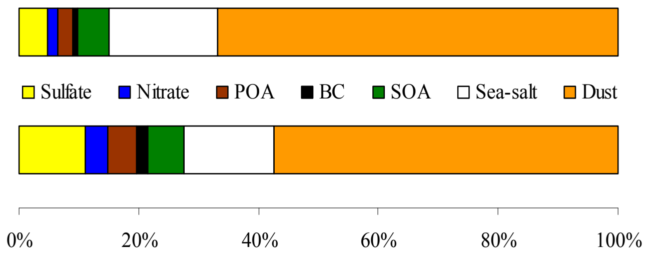

Figure 1. Contribution to the total aerosol optical depth for each one of the aerosol species (annual global mean) for the preindustrial (top; AOD 0.084) and present (bottom; AOD 0.102) atmospheres. Ammonium aerosol is included in the nss-sulfate and nitrate contribution (Figure from Tsigaridis *et al.* [2006]).

The contribution of each species has changed since preindustrial times, with the most important change being the more than doubling of the nss-sulfate, nitrate, and BC contributions to the AOD, resulting from an increase of their sources and thus their atmospheric load (Table 1). The POA contribution to the AOD has increased by 86 %. The increase in BC contribution by a factor of 2.7 is higher than that of POA due to BC lower solubility (reflected by the insoluble/soluble ratio in the emitted amounts compared to that of POA), which results in relatively less effective removal and thus higher burden (and higher AOD) compared to that of POA during the present day. Since sea-salt and dust have equal burdens during the present and preindustrial simulations, their relative contribution to the total AOD has decreased nowadays by about 15 % due to the increase of the other aerosol components.

Although according to these model simulations, the chemical production of SOA has more increased by more than 50 % since pre-industrial time due to the increase in oxidants and in pre-existing particles that act as substrate for condensational sink of semi-volatiles, the SOA burden increases at the present day, but not so notably as the mainly anthropogenic aerosols. This is attributed to an enhanced removal of these aerosols from the atmosphere. Therefore, SOA relative contribution to the total AOD is only 11% higher nowadays.

Table 1. Global annual average aerosol burden for the present and preindustrial simulations and comparison with the literature. All units are Tg. (for references see Tsigaridis *et al.* [2006])

	This work		Previous works	
Aerosol type	Present	Pre-industrial	Present	Pre-industrial
Nss-sulfate	1.05	0.40	0.29-2.55[1]	0.10-0.58[2]
Ammonium	0.35	0.12	0.33-0.54[3,b]	0.12[3]
Nitrate	0.31	0.12	0.04-0.63[4]	0.10-0.18[5]
MSA	0.22	0.27		
SOAb	0.75	0.64	0.01-1.6[6]	0.06-0.6[7]
SOAa	0.05	0.00	<0.01-0.03[8]	
POA	0.60	0.27	0.77-1.48[9]	0.096-0.11[10]
total OA	1.40	0.91	0.24-2.21[11]	0.03-0.17[12]
BC	0.12	0.03	0.11-0.29[13]	0.011-0.02[10]
Sea-salt	4.45	4.45	0.97-13.21[14]	0.96[15]
Dust	19.60	19.60	7.9-35.9[16,c]	

The percent contribution of the various components to the AOD per continent is shown in Figure 2 both for the present and preindustrial atmospheres. As expected, the strongest changes have occurred over the most industrialized continents, namely North America, Europe and Asia. The anthropogenic emissions of SO_2 and NO_x have enhanced the nss-sulfate and nitrate aerosols, resulting in higher contribution to the AOD. In areas with strong deforestation, namely North and South America, Africa, and Indonesia – Oceania, the increase in the relative contribution of primary carbonaceous aerosols to the total AOD is also important.

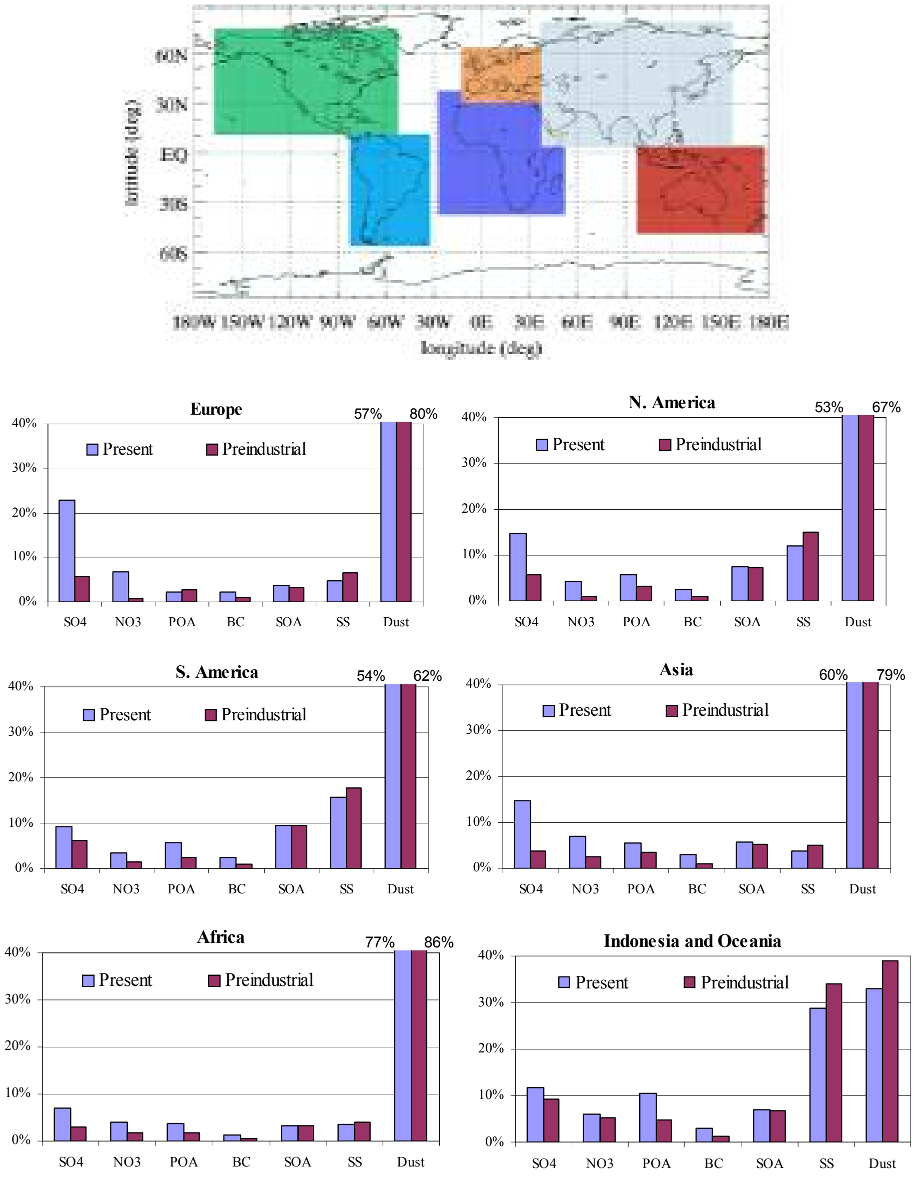

Figure 2. Map: Continental box regions definition for the AOD comparison. The African box overlaps with the European and the Asian ones. Charts: Relative percentage contribution of aerosol components per continent for the present and preindustrial atmospheres. The effect of water is included to each one of the aerosol components. The continental mean AOD values for the present and preindustrial simulations respectively are: Europe: 0.204, 0.146; N. America: 0.092, 0.074; S. America: 0.099, 0.087; Asia: 0.179, 0.136; Africa: 0.311, 0.279; Indonesia and Oceania: 0.071, 0.060. SS means sea-salt.

Concluding remarks

According to our 3-D global model simulations that are based to actual kinetic knowledge on SOA formation, SOA contributes by 17 % to the aerosol burden, when neglecting sea-salt and dust that are the major contributors and are of natural origin. This translates to a contribution to the total AOD that regionally can reach 10 %. However, SOA impact on climate can be larger when considering the amplification of the absorption of light by black carbon due to the presence of organics [Schnaiter *et al.*, 2003] as well as the potential of SOA components to activate condensation nuclei [Giebl *et al.*, 2002].

Acknowledgments

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Secondary Organic Aerosol Formation from Acetylene: Seed, Acid and RH Dependence of Glyoxal Uptake to Aerosols

Contribution to the ACCENT Workshop on Volatile Organic Compounds: Group 3

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Introduction

Secondary organic aerosol (SOA) formation from partitioning of semi-volatile and non-volatile oxidation products of volatile organic compound (VOC) oxidation is being parameterized in state-of-the-art atmospheric models from empirical fits to simulation chamber data [Odum *et al.* 1996; Pankow 1994]. Conditions in these chambers approximate the polluted atmosphere to the best possible extent, *i.e.* with respect to VOC/NOx ratios, NOx concentrations, temperatures, the pool of condensable species produced, OH-radical concentrations, and light conditions. However, it is recently being questioned if such models accurately simulate SOA formation in the atmosphere. Larger than predicted SOA is found in different and large compartments of the atmosphere [DeGouw *et al.* 2005; Heald *et al.* 2005; Johnston *et al.* 2006; Volkamer *et al.* 2006a], including the urban and free troposphere (Figure 1). The reasons for these differences are presently not clear, and subject to ongoing debate.

In Mexico City, direct and highly time-resolved measurements of glyoxal [Volkamer *et al.* 2005a] and SOA [Zhang *et al.* 2005] were accomplished by means of open-path Differential Optical Absorption Spectroscopy (DOAS) and Aerosol Mass-Spectrometry (AMS). Glyoxal is a first generation oxidation product from aromatic VOC [Volkamer *et al.* 2001; Volkamer *et al.* 2005b]. The coincident formation of glyoxal and SOA demonstrates that uncertainties in our understanding of SOA formation exist on very short time-scales of oxidation, comparable to time-scales probed in simulation chambers. Contrary to previous believe, first-generation anthropogenic oxidation products form SOA in the urban atmosphere [Volkamer *et al.* 2006a].

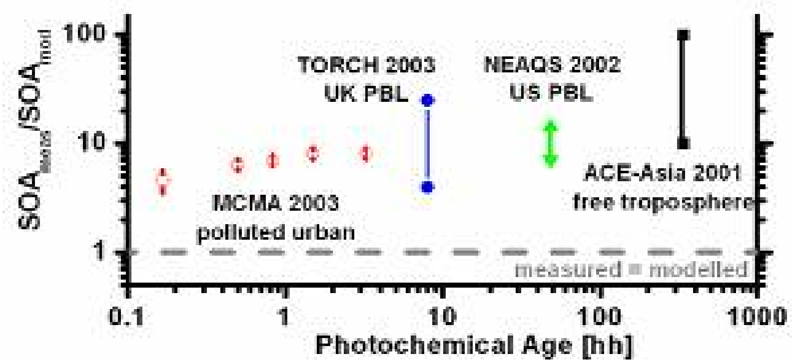

Figure 1. Differences in predicted and modelled SOA formation from four field campaigns; adopted from Volkamer *et al.* [2006a].

We here corroborate our previous conclusion that volatile carbonyls like glyoxal play an important role in the formation of SOA [Volkamer *et al.* 2006b], and present results from specific laboratory experiments on SOA formation from the oxidation of acetylene, the lightest non-methane hydrocarbon (NMHC).

SOA formation from glyoxal

Glyoxal is formed from the oxidation of aromatic VOC, alkenes (including isoprene) and oxygenated compounds from anthropogenic and biogenic sources [Calvert *et al.* 2000; Volkamer *et al.* 2005c]. In an urban atmosphere like Mexico City, the oxidation of acetylene accounts for about 10 % to the overall glyoxal sources, with the remaining 90 % being mostly due to the oxidation of other VOCs. Rapid gas-phase reaction with OH-radicals and photolysis limit the atmospheric lifetime of glyoxal to few hours [Volkamer *et al.* 2005a]. Previous contradictory findings exist with regard to the importance of aerosols as a sink for glyoxal. On inorganic seed glyoxal uptake had been suggested to be irreversible [Liggio *et al.* 2005] or to be reversible [Kroll et al. 2005]. Also the role of acid-catalysis to enhance the uptake of glyoxal to aerosols [Jang *et al.* 2002] is recently being disputed [Kroll *et al.* 2005; Volkamer *et al.* 2006b].

Experimental

Acetylene is the lightest hydrocarbon after methane. The oxidation products from acetylene are very volatile. Partitioning to aerosols is not expected as the result of physical processes (condensation, sorption into an organic liquid). The products of acetylene are summarized together with their respective Henry's law coefficients [Sander *et al.* 2006; Kroll *et al.* 2005] in Table 1.

Table 1. Products formed in the acetylene/CHONO/NO_x/light system, and their respective effective Henry's law coefficients for partitioning to an aqueous aerosol phase.

Product	C	Conc. [ppb]	$H(298K)_{eff}$ [$M\ atm^{-1}$]	Conc × H_{eff} [rel. units]
CHOCHO	2	100	$2.6\ 10^{7}$	1
HCHO	1	320	$3.2\ 10^{3}$	$3.5\ 10^{-4}$
HCOOH	1	61	$8.9\ 10^{3}$	$2.0\ 10^{-4}$
CH_3NO_3	1	6	2.0	$4.6\ 10^{-9}$
CO	1	93	$9.8\ 10^{-4}$	$3.5\ 10^{-11}$
HNO_3	0	28	$2.1\ 10^{5}$	$2.3\ 10^{-3}$
HONO	0	300	50	$5.8\ 10^{-6}$

A series of smog chamber experiments was performed using acetylene + OH as a source of glyoxal. SOA formation was monitored using Aerosol Time of Flight Mass Spectrometry (ATOFMS), High-resolution Time of Flight Mass Spectrometry (HR-TOF-AMS), Scanning Mobility Particle Sizing (SMPS), and selected gas-phase instrumentation for NOx, CO. CH_3ONO/NO/UV-light was used as a well defined source for OH-radicals. Experiments were conducted using humidified air in the presence of various types of seed aerosols, *e.g.* $(NH_4)_2SO_4$, NH_4HSO_4, succinic acid, mixed organic/inorganic seeds, and $(NH_4)_2SO_4$ seed acidified with sulphuric acid at variable RH (15 % < RH < 85 %), *i.e.* above and below delinquesence RH.

Results

Significant SOA mass is formed from acetylene on all seeds investigated (Figure 2). Table 1 demonstrates that acetylene is a clean source for glyoxal to the aqueous aerosol phase. No continued growth is observed after the experiment, indicating the glyoxal uptake to the seed aerosol proceeds via a reversible mechanism. This finding is in contrast to the results obtained by [Liggio *et al.* 2005], and qualitatively confirm the observations by [Kroll *et al.* 2005]; we were able to reproduce the quantitative results of Kroll *et al.* within 30 %. Our study allows significantly improved conclusions about the time-scale over which the uptake of gaseous glyoxal to the aqueous aerosol phase reaches equilibrium. An upper limit is determined to be less than 1 min.

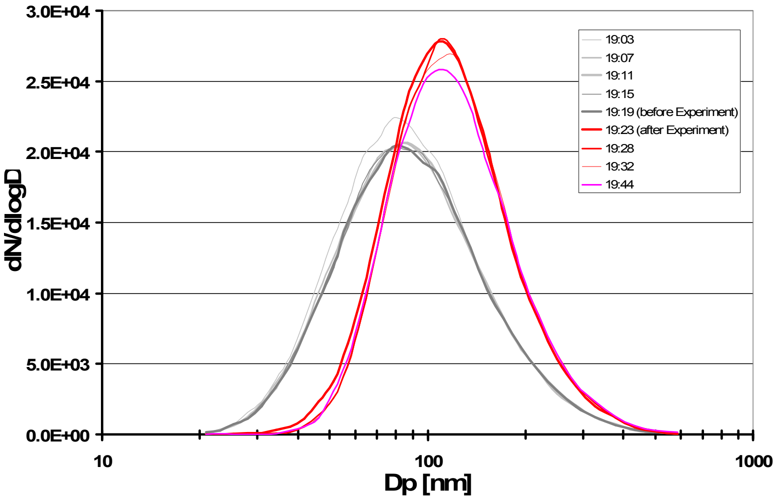

Figure 2. SOA formation in the oxidation of acetylene. The size distribution of the seed aerosol in the absence of glyoxal (grey lines) is shifted towards larger diameters in the presence of glyoxal (red lines). No continued growth is observed indicating reversible glyoxal uptake for all seeds studied.

Similar and higher uptake is observed for organic aerosol seeds, suggesting that the mechanism for glyoxal uptake to aerosols is unlikely to be controlled by ionic strength of the particles, as had been suggested by [Kro*ll et al.* 2005]. The lack of a correlation of glyoxal uptake to particles with ionic strength is also consistent with glyoxal-budget considerations from field observations [Volkamer *et al.* 2005d].

We observe a correlation of glyoxal uptake and RH for all seeds investigated. The effective Henry's law constant varied by more than a factor of 20 over the RH range studied for organic/inorganic seeds (15 % < RH < 85 %). Higher glyoxal uptake is observed at elevated RH. This finding indicates the crucial role of aerosol liquid water for SOA formation from glyoxal.

The effective Henry's law constant was further observed to depend on the chemical composition of the seed. At RH = 50 %, the effective Henry's law constant varied by more than a factor of five for the studied seeds. It was observed highest for mixtures of organic/inorganic seed, and lowest for pure organic and acidified organic/inorganic seeds. We do not see any indication for acid-enhancement of glyoxal uptake in our experiments. Rather on the contrary, indications were found that moderate additions of acid reduce the uptake of glyoxal; indicating possible competition of acid and glyoxal for aerosol liquid water.

Discussion and atmospheric implications

There is presently more than 40 hydrocarbon precursors for glyoxal identified in the atmosphere [Volkamer *et al.* 2005c], including isoprene. The formation of SOA from the oxidation of acetylene, the lightest hydrocarbon after methane, can not be explained in terms of physical processes like condensation of partitioning of oxidation products in any organic aerosol phase (the vapour pressure of glyoxal is several Pa at a temperature of –40 °C). Our observations are compatible with reversible heterogeneous reactions of glyoxal in the aqueous phase, in line with observations by [Kroll *et al.* 2005], and in contrast to observations by [Liggio *et al.* 2005]. We do not find any indication for the "salting-in" mechanism proposed by [Kroll *et al.* 2005]. Similar uptake of glyoxal is observed for aqueous inorganic and organic seeds of very different ionic strength, indicating that ionic strength is unlikely to control the pathway that binds glyoxal to aerosols. We observe a strong dependence of glyoxal uptake on the type of seed aerosol. For mixed organic/inorganic seeds the effective uptake of glyoxal is about a factor of three to five higher than for pure ammonium sulphate seed. A strong RH dependence is observed for mixed organic/inorganic seeds (more than a factor of 20 over the RH range studied), suggesting an important role of aerosol liquid water. The liquid water content in our study is controlled by the inorganic components of the seed. Further, we do not find any indication for enhanced effective uptake of glyoxal to mixed organic/inorganic seed aerosols that were acidified with sulphuric acid. The detailed mechanism of glyoxal processing in particles remains to be elucidated.

The upper limit effective Henry's law constant of glyoxal in aerosols is found 2.2 10^8 M atm^{-1} for mixed inorganic/organic seed at high RH. This is about three orders of magnitude higher than the effective Henry's law constant of glyoxal in liquid water. The liquid water content of clouds is about four orders of magnitude larger than that of aerosols. The observed effective uptake of glyoxal to aqueous inorganic/organic aerosols is thus high enough to compensate for most of the lower liquid water content associated to aerosols; a significant portion of glyoxal will partition to the aqueous aerosol phase. Under typical concentrations of the semi-polluted atmosphere, (gas-phase glyoxal 400 ppt, aqueous aerosol 10 $\mu\text{g m}^{-3}$) up to 52 ng m^{-3} of glyoxal related SOA are formed. This corresponds to about 25 % of the glyoxal is present in the aerosol phase.

Previous studies had been suggested that glyoxal processing is a source of oxalic acid, and hence SOA, in clouds [Ervens *et al.* 2004; Lim *et al.* 2005; Warneck *et al.* 2005]. As aerosols are several orders of magnitude more concentrated solutions compared to clouds, a strong effect on oxidation rates is expected, and requires further investigation. Finally, state-of-the-art models predict SOA formation in terms of the condensation of non-volatile compounds or the partitioning of semivolatile organic gases into the liquid organic aerosol phase [Odum *et al.* 1996; Pankow 1994]. These models fall short to explain atmospheric SOA observations (see Figure 1). The chemistry of the aqueous phase of aerosols is currently not represented in these models. Current representations of gas-to-particle partitioning in terms of volatility driven partitioning into the liquid organic aerosol phase needs to be expanded towards a solubility and volatility based parameter space of mixed aqueous/organic/inorganic aerosols and multiphase systems.

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12. Appendices

A. List of Participants

T & T P

AT2

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

Volatile Organic Compounds in the Polluted Atmosphere
The 3rd ACCENT Barnsdale Expert Workshop

List of Participants

Group 1 — Emissions of VOC – anthropogenic and biogenic

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Group 2 — Uncertainties in local, regional and global processing of VOC

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Group 3 Production, properties, and removal of SOA – fate of VOC

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Organisation

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Peter Borrell, P&PMB Consultants
Newcastle-under-Lyme
October 2006

B. Programme

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

Volatile Organic Compounds in the Polluted Atmosphere
The 3rd ACCENT Barnsdale Expert Workshop

Programme

Discussion groups

1. Emissions of VOC – anthropogenic and biogenic
2. Uncertainties in local, regional and global processing of VOC
3. Production, properties, and removal of SOA – the fate of VOC

Programme

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

Monday, 30th October 2006		
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)* The aims and organisation of the meeting	***Chair: Claire Granier*** Paul Monks
14.15	Production, properties, and removal of SOA – the fate of VOC *Topic 3 plenary*	David Simpson
15.00	Formulation of Topic 3 issues	Maria Kanakidou
15.30	Uncertainties in atmospheric VOC chemistry - what don't we know already? *Topic 2 plenary*	Jonathan Williams
16.15	*Tea (Edith Weston Common Room)*	
		Chair: Tony Cox
16.45	Formulation of Topic 2 issues	Ron Cohen
17.15	Emissions of VOC – anthropogenic and biogenic *Topic 1 plenary*	Francesco Loreto
18.00	Formulation of Topic 1 issues	Jürgen Kesselmeier
18.30	Close	
from 18.45	*Mixer (Rutland room)*	
19.30	*Dinner (Osprey room)*	

Tuesday, 31st October 2006		
9.00	Group Discussions, Session 1 *Group rooms:* 1. *Rockingham* 2. *Hambleton* 3. *Whitwell*	
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. 1st November 2006		
09.00	Start *(Langham Room)*	***Chair: Paul Monks***
	Emissions of VOC – anthropogenic and biogenic *Topic 1 report*	Nicola Blake
09.30	General discussion on Topic 1	Jürgen Kesselmeier, Nicola Blake
10.00	Uncertainties in local, regional and global processing of VOC *Topic 2 report*	John Wenger
10.300	General discussion on Topic 2	Ron Cohen, John Wenger
11.00	*Coffee (Edith Weston Common room)*	
		Chair: John Burrows
11.30	Production, properties, and removal of SOA – the fate of VOC *Topic 3 report*	Rainer Volkamer
12.00	General discussion on Topic 3	Maria Kanakidou, Rainer Volkammer
12.30	What have we learned and where do go from here?	Paul Monks
12.45	*Lunch (Osprey room)*	
13.30	*Close*	

C. Briefing Sheets for Chairs, Rapporteurs, Speakers and Participants

Transport and Transformation of Pollutants (T&TP),
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AT2

Briefing Sheet

1. Meeting Arrangements
    - Aims of the workshop
    - Organisation
    - Outcome of the Workshop
    - Contributions
    - Group Chairs and Rapporteurs
    - Plenary Speakers

2. Roles of Speakers, Chairs, Rapporteurs and Participants
    - Role of the Plenary Speakers
    - Role of the Chairs
    - Role of the Rapporteurs
    - Role of the Participants

1. Meeting Arrangements

Aims of the workshop

The aim of the expert meeting is:

* to identify and review the key uncertainties in our current understanding of the emission to the atmosphere, processing within the atmosphere and removal of VOC from the atmosphere; and

* to provide a basis for future collaborative research priorities in this area.

Organisation

The meeting will be organised around guided discussions on three topics.

1. Emissions of VOC – anthropogenic and biogenic.
2. Uncertainties in local, regional and global processing of VOC.
3. Production, properties, and removal of SOA – the fate of VOC.

The meeting will start with invited review papers on each topic 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.

Outcome of the Workshop

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

Contributions

All invited participants will be 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.

Group Chairs and Rapporteurs

	Chair	Rapporteur
Group 1	Juergen Kesselmeier	Nicola Blake
Group 2	Ron Cohen	John Wenger
Group 3	Maria Kanakidou	Rainer Volkamer

Plenary Speakers

Group 1	Francesco Loreto	Emissions of VOC – anthropogenic and biogenic
Group 2	Jonathan Williams	Uncertainties in atmospheric VOC chemistry - what don´t we know already?
Group 3	David Simpson	Production, properties, and removal of SOA – the fate of VOC

2. Roles of Speakers, Chairs, Rapporteurs and Participants

Role of the Plenary Speakers

- *Prior to the meeting*, speakers might wish to consult the Chair and Rapporteur of 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 by all the groups.
- 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 a 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/AVOC/AVOC_Contribution_template.doc

Role of the Chairs

- *Prior to the meeting*, Chairs might like to consult with the Plenary Speaker and Rapporteur of 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 groups 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.
- *Prior to the meeting*, you might like to contact your fellow rapporteurs, to agree a suitable format for the reports that you will each make.
- *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.
- 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/AVOC/AVOC_Contribution_template.doc
- It would be appreciated if the rapporteurs could work up their final version and send it to *Peter Borrell* before the *30th November 2006*.

Role of the Participants

- The principal role is to participate! *i.e.* to contribute to the discussion on the various questions.
- *Prior to or at the meeting*, they should provide an electronic version of their likely voxbox 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/AVOC/AVOC_Contribution_template.doc
- Contributions 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 Chairman of the group session, to make several voxbox contributions.

Peter Borrell, P&PMB Consultants
Newcastle-under-Lyme
September 2006

D. Group Photographs

photographs: Patricia Borrell; Marigold Penkett