

A Conference in the Grand Hotel Bernardin, Portoroz, Slovenia
April 14th - 17th 2009

Tropospheric Chemistry

held in the frame of

INTROP

Interdisciplinary Tropospheric Research: from the Laboratory to
Global Change



An ESF Scientific Programme



Supported by EUROCHAMP

Tropospheric Chemistry

Grand Hotel Bernardin, Portoroz, Slovenia, April 14th – 17th 2009.

PROGRAMME

As the INTROP conferences before, this meeting aims at being discussion-oriented with scientists exchanging ideas through their interaction on tropospheric chemistry and some of its current and evident frontline research topics. Each topic will be introduced by invited lecturers who are expected to address general and specific questions.

There are talks of 30 and 45 minutes duration including 10 and 15 minutes discussion, respectively. There is additional discussion time at the end of the presentations of each topic area.

On each day, discussion leaders will motivate the discussion and prepare informal late evening discussions.

There will be a poster session throughout the whole conference.

Tuesday, April 14th 2009

08.00 - 14:00	Arrival and Registration	
12:00 – 14:00	Buffet Lunch	
14:00	Start of Conference	
14:00 – 14:10	Welcome by Edvard Kobal, SZF (Slovenian Science Foundation)	
14:10 – 14:20	Welcome by ESF	Didier Hauglustaine
14:20 – 14:30	Welcome by the INTROP coordinator	Christian George
14:30 – 14:45	Organisational and local issues	H. Herrmann, I. Grgic

Topic Area 1: Prediction of the atmospheric fate of complex pollutants

Discussion Leader: Claus Nielsen

14:45 – 15:30	Ian Barnes Aromatic Hydrocarbon Gas Phase Photooxidation Mechanisms: Recent Advances and Ongoing Work
15:30 – 16:15	Georges LeBras Recent Advances in Gas Phase Chemistry influencing the Oxidative Capacity of the Troposphere

16:15 – 16:45	Coffee
16:45 – 17:15	Eric Villenave OH-initiated Oxidation of Monoterpenes: the Importance of the Abstraction Pathway
17:15 – 17:45	Dwayne Heard Field measurements of OH and HO ₂ radicals: Insights into novel Mechanisms
17:45 – 18:15	Mike Pilling Developments in the Master Chemical Mechanism (MCM v3.1)
18:15 – 18:45	Discussion on TA 1
19:30	Dinner

Topic Area 2: Aerosols and global change

Wednesday, April 15th 2009

- Overviews –

- Discussion Leader: Yinon Rudich -

08:30 – 09:15	Jason Surrat Recent Results on Secondary Organic Aerosol (SOA) Formation at Caltech: Photooxidation of Polycyclic Aromatic Hydrocarbons (PAHs) and Reactive Uptake of Glyoxal
09:15 – 10:00	Gunnar Myhre Consistency between satellite-derived and modelled Estimates of the direct Aerosol Effect
10:00 – 10:30	Coffee

- Biological systems and Aerosols -

10:30 – 11:15	Astrid Kindler-Scharr Secondary Organic Aerosol Formation from boreal Tree Emissions
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- Aging, Processing and Functionalisation -

11:15 – 12:00	Neil Donahue Oxidized Organic Aerosol and Emissions: How do we get there from here?
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- 12:00 – 12:30 **Magda Claeys**
Molecular Characterization of Secondary Organic Aerosol from Isoprene and Monoterpenes
- 12:30 – 13:00 **Yoshiteru Iinuma**
Formation of Organosulphates from reactive Uptake of Monoterpene Oxides
- 13:00 – 14:30 Lunch

Organic coatings and Surface (photo)chemistry
- Discussion Leader: Christian George -

- 14:30 – 15:15 **Doug Tobias**
Molecular Simulation of the Surfaces of Aged Sea Salt and Organic Aerosol Particles
- 15:15 – 16:00 **Barbara d'Anna**
Photochemistry at Interfaces: the Effect of Light on Trace Gases Uptake
- 16:00 – 16:30 **James Donaldson**
Atmospheric Chemistry at aqueous Surfaces: What have we learned and where are we going?
- 16:30 – 17:00 Coffee

Tropospheric Aqueous Phase Chemistry
- Discussion Leader: Hartmut Herrmann -

- 17:00 – 17:45 **Michael Hoffmann**
Atmospheric Chemistry at Air-Water Interfaces
- 17:45 – 18:15 **Laurent Deguillaume**
Could Micro-organisms play an active role in Atmospheric Chemistry ?
- 18:15- 18:45 Discussion on TA 2
- 19:30 Dinner
- 20:30 Poster Pub

Thursday, April 16th 2009

- *Advanced measurement techniques* -
- Discussion Leader: Dwayne Heart -

- 08:30 – 09:15 **Johannes Orphal**
Incoherent Broad-Band Cavity-Enhanced Spectroscopy for
Atmospheric Studies
- 09:15 – 09:45 **Armin Hansel**
High Resolution PTR-TOF: A New Instrument for Organic Compound
Measurements
- 09:45 – 10:30 **Frank Drewnick**
On-line Aerosol Measurements – Results from Recent Field Campaigns
- 10:30 – 11:00 Coffee

Topic Area 3: Remote sensing - Complex Modelling
- Discussion Leader: Johannes Orphal -

- *Remote sensing* -

- 11:00 – 11:45 **Ilan Koren**
A Superposition of Microphysics and Absorption Effects of Aerosol on
Clouds
- 11:45 – 12:15 **Oleg Dubovik**
Aerosol Remote Sensing: Principles, Evolution and Perspectives.
- 12:15 – 13:45 Lunch

- *Complex Modelling* -
- Discussion Leader: Mike Pilling -

- 13:45 – 14:30 **Elina Marmer**
Global Modeling: Applications at the Joint Research Centre
- 14:30 – 15:00 **Johann Feichter**
Feedbacks between Aerosol Cycles and Climate
- 15:00 – 15:30 Discussion on TA 3
- From 15:30 Excursion Time
- 19:30 Dinner

Friday, April 17th, 2009

Topic Area 4: Technologies and the Future

- Discussion Leader: Cornelius Zetzsch -

- *Technologies* -

- 08:45 – 09:15 **Peter Wiesen**
EUROCHAMP-2: Atmospheric Simulation Chambers for Studying
Atmospheric Chemical Processes
- 09:15 – 10:00 **Claus Nielsen**
Atmospheric Degradation of Amines – Results from a Screening Study
- 10:30 – 11:00 Coffee

- *Final Panel Discussion* -

- 11:00 – 12:00 Panel Discussion : Where do we go from here ?
- 12:00 End of Conference
- 12:00 – 13:00 Bufett Lunch and Departure

ABSTRACTS of TALKS

Aromatic Hydrocarbon Gas Phase Photooxidation Mechanisms: Recent Advances and Ongoing Work

Ian Barnes

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Aromatic hydrocarbons (benzene, toluene, xylenes: BTX) are emitted to the atmosphere from traffic, various industrial processes and from the use of organic solvents. They contribute up to 44% of the volatile organic compounds (VOCs) observed in cities in different parts of the world. Their photooxidation contributes significantly to the formation of urban photochemical smog. Aromatic hydrocarbons together with alkenes rank as the most important compound classes with respect to photooxidant formation. Detailed mechanisms have been developed to describe the photooxidation of the aromatics and are used to simulate experimental observations in photoreactors. Such simulations have revealed many shortcomings in the present mechanisms, e.g. they under-predict the OH radical and over-predict the O₃ production.

Aromatic hydrocarbons are mainly degraded in the troposphere through reaction with OH-radicals. The oxidation occurs via several reaction channels that result in either ring-opening or ring-retaining products. There are two ring-retaining routes that produce hydroxylated aromatics and aromatic aldehydes as first-generation products and these are fairly well understood. The chemistry of the ring-opening routes is still very speculative in nature and many different ring-opening routes have been proposed and probed experimentally.

Recent work on elucidating the gas phase photooxidation mechanisms of aromatic hydrocarbons will be reviewed with particular attention being given to the ring-opening routes producing dicarbonyl compounds. Work currently ongoing in different areas of the photooxidation mechanism of aromatic hydrocarbons will be highlighted.

Recent advances in gas phase chemistry influencing the oxidative capacity of the troposphere

Georges Le Bras

CNRS ICARE, Orléans

Studies of gas phase chemistry in different laboratories have recently provided new kinetic and mechanistic data that appear to have a significant (or potentially significant) impact on the oxidative capacity of the troposphere, mainly by controlling the tropospheric concentrations of the OH radicals at local, regional or global scales. The studied reactions are sources or sinks of HO_x (OH, HO₂) radicals which are rapidly inter-converted. The reactions to be presented include in particular photolysis of carbonyls (formaldehyde, acetone, ...), OH forming channel in the reactions of organic peroxy radicals, RO₂, with HO₂ (CH₃C(O)O₂ + HO₂,...), OH formation in the excited NO₂ with H₂O (questionable), HNO₃ forming channel in the HO₂ + NO reaction and water vapour effect, and nitrate formation in RO₂ + NO reactions.

Field measurements of OH and HO₂ radicals: Insights into novel mechanisms

Dwayne Heard

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

Field measurements of the concentrations of OH and HO₂ radicals and comparison with box model calculations are a sensitive method to probe the details of tropospheric mechanisms. Recently, measurements of a new parameter, the OH reactivity, have provided an additional target for models, and have demonstrated the existence of missing OH sinks, both in forested and anthropogenically influenced environments. The product of the measured OH reactivity and OH concentration gives the chemical turnover rate, and application of the steady-state approximation enables the total rate of production of OH to be measured, providing another target for models. In this way, the existence of significant missing sources of OH has also been demonstrated.

In this presentation, the focus will be on data measured by the Leeds FAGE group and other groups in the tropics during ground- and airborne-based field campaigns. Environments include (a) the Cape Verde Islands, representative of the remote tropical marine boundary layer, (b) continental West Africa impacted by monsoonal and anthropogenic influences, (c) in and above the rainforests of Suriname and Borneo, characterised by high concentrations of biogenically emitted hydrocarbons, and (d) Mexico City and the Pearl River Delta, China, which are heavily influenced by anthropogenic emissions. At Cape Verde, bromine and iodine chemistry play a crucial role in the conversion of HO₂ to OH and in the destruction of ozone, whereas in other tropical regions there are both significant missing sinks and sources for OH. An efficient recycling mechanism forming OH from reactions of RO₂ and HO₂ appears to be missing in current models for biogenically influenced regions. If time permits, some recent results from laboratory and chamber studies regarding OH sources will be discussed.

Developments in the master chemical mechanism (MCM v3.1)

M. J. Pilling

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK

The master chemical mechanism is an almost explicit chemical mechanism for the oxidation of 135 volatile organic compounds. It is constructed on the basis of a published protocol (see references below) and contains rate coefficients based on evaluated, published or estimated rate coefficients. It contains over 5000 species and over 15000 reactions. The talk will summarise:

- The basis of the MCM and of its construction.
- The functionality of the MCM website
- Applications: radical chemistry, SOA formation, reduced mechanism evaluation, policy development.
- The use of chamber experiments to evaluate the MCM and developments within EUROCHAMP to extend the basis of this evaluation.
- Recent and planned developments:
 - Direct linkage to the IUPAC evaluated IUPAC database allowing automatic updates of rate data.
 - Proposed linkage to condensed phase mechanism.
 - Incorporation of new biogenic species.
 - Lumped version.
 - New retro-extraction tool.
 - On line box model for use of MCM.
 - Electronic notebook for searchable mechanism evaluation experiments.

References

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OH-initiated Oxidation of Monoterpenes: the Importance of the Abstraction Pathway

C. Rio, J. C. Loison, F. Caralp, P. M. Flaud and E. Villenave

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Secondary Organic Aerosol (SOA) formation in the atmosphere is described as a mass transfer of volatile organic compound oxidation products with low vapour pressures in particular phases. Among the different aerosol components, the SOA represent an important fraction, but, the fundamental processes governing their physics and chemistry in the atmosphere are poorly understood. So it is important to characterize and understand the mechanisms of their formation.

It is well-known that atmospheric oxidation of monoterpenes is an important process in tropospheric SOA formation. Consequently, the identification and quantification of reaction products from the oxidation of monoterpenes in the gas phase have been receiving great attention over the past years.

However, the atmospheric degradation leads to the formation of a plethora of reaction products and proceeds through a very complex mechanism that is still not fully characterised.

In our study, we have focused on SOA formation from OH + monoterpene reactions and more precisely on the primary oxidation steps of γ -terpinene and d-limonene by OH radicals. Indeed, the primary reaction of monoterpenes with hydroxyl radicals can in principle occur by two reaction pathways: OH-addition and H-abstraction. In this work, we have determined branching ratios of these reactions. Although there seems to be a consensus in the literature that OH-monoterpene reactions proceed almost exclusively by addition, several measurements have shown that in some case H-abstraction can represent up to 30% of the total reaction rate constant. Therefore it is necessary to determine this branching ratio in order to know, in particular, the main peroxy radicals formed and propose a mechanism for the gas phase oxidation of terpene by hydroxyl radicals.

(γ -terpinene + OH) and (d-limonene + OH) reactions have been studied i) at atmospheric pressure, using laser photolysis coupled with UV absorption radical detection, and ii) at low pressure, using discharge-flow reactor coupled to mass spectrometry. Therefore, it has been possible to measure the branching ratios between the abstraction and addition channels at different pressures and to discuss on H-abstraction importance for all reactions of monoterpenes with hydroxyl radicals.

This work has shown that, contrary to the results of the available literature, H-abstraction is a significant reaction pathway for the reaction of monoterpenes with hydroxyl radical. Therefore, oxidation products resulting from the H-abstraction should not be neglected in the mechanisms describing the reaction of monoterpene + OH and SOA formation.

Recent Results on Secondary Organic Aerosol (SOA) Formation at Caltech: Photooxidation of Polycyclic Aromatic Hydrocarbons (PAHs) and Reactive Uptake of Glyoxal

Jason D. Surratt¹, Arthur W. H. Chan¹, Puneet S. Chhabra¹, Kathryn E. Kautzman¹, Melissa M. Galloway², Man N. Chan³, John D. Crouse¹, Andreas Kürten³, Paul O. Wennberg^{3,4}, Frank N. Keutsch², Richard C. Flagan^{1,3}, and John H. Seinfeld^{1,3}

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When accounting for known volatile SOA precursors, state-of-the-art SOA models consistently underestimate the amount of SOA measured in many urban locations, indicating that significant sources of SOA are not yet identified or well characterized. During this presentation, recent work conducted in the Caltech dual 28-m³ chambers will be discussed, which has been aimed at better understanding urban SOA sources.

First, SOA formation from the gas-phase photooxidation of naphthalene, 1-methylnaphthalene (1-MN), and 2-methylnaphthalene (2-MN) under both high- and low-NO_x conditions, as well as 1,2-dimethylnaphthalene (1,2-DMN) under high-NO_x conditions, will be discussed. Under high-NO_x conditions and aerosol mass loadings between 10 and 40 µg m⁻³, the SOA yields (mass of SOA per mass of hydrocarbon reacted) ranged from 0.19 to 0.30 for naphthalene, 0.19 to 0.39 for 1-MN, 0.26 to 0.45 for 2-MN, and constant at 0.31 for 1,2-DMN. Under low-NO_x conditions, the SOA yields were measured to be 0.73, 0.68, and 0.58, for naphthalene, 1-MN, and 2-MN, respectively. The SOA was observed to be semivolatile under high-NO_x conditions and essentially nonvolatile under low-NO_x conditions. When applying these measured yields to estimate SOA formation from primary emissions of diesel engines and wood burning, PAHs are estimated to yield 3-5 times more SOA than light aromatic compounds. PAHs can also account for up to 54% of the total SOA from oxidation of diesel emissions, representing a potentially large source of urban SOA.

To conclude, we will discuss the role of the reactive uptake of glyoxal, a common oxidation product of both biogenic and anthropogenic VOCs, in forming SOA. In order to gain further insight into the processes controlling SOA formation involving glyoxal, uptake of glyoxal onto wet ammonium sulfate seed aerosol was examined under both dark and irradiated conditions. Under dark conditions, glyoxal oligomer formation and overall organic growth were found to be reversible. Organic fragments from at least glyoxal dimers and trimers were observed in the aerosol phase under both dark and irradiated conditions. Analysis of the high-resolution time-of-flight aerosol mass spectra provides evidence for irreversible formation of carbon-nitrogen (C-N) compounds in the aerosol. These compounds were identified to be imidazoles formed by reaction of glyoxal with condensed-phase ammonia. Organosulfates were not detected under dark conditions (even with highly acidified sulfate seed aerosol), indicating that the previously proposed acid catalyzed formation mechanism is not viable for the prior tentatively proposed glyoxal sulfate found in both laboratory-generated isoprene and ambient SOA. However, active oxidative photochemistry, similar to that found in cloud processing, was identified within aerosol during irradiated experiments. Glycolic acid sulfate, carboxylic acids, and organic esters were detected within the irradiated aerosol. Our study suggests that both C-N compound formation and photochemical processes should be considered in models of SOA formation via glyoxal. Our work shows the importance of including SOA production from gas-phase reactions of PAHs and from reactive uptake of glyoxal in current atmospheric models to reconcile model-observation discrepancies.

Consistency between Satellite-derived and modelled Estimates of the direct Aerosol Effect

G. Myhre

Center for International Climate and Environmental Research – Oslo, CICERO

The radiative forcing of the direct aerosol is estimated to -0.5 Wm^{-2} in the latest IPCC assessment with a large uncertainty range. A main reason for the large uncertainty range is the difference between estimates from global aerosol models and observational based methods. Recent developments for the estimates from the global aerosol models and observational based methods will be presented, such as inclusion of nitrate and secondary organic aerosols in model estimates. It will be discussed effects of external and internal mixing of black carbon with other aerosol types. Effects of updates in the MODIS satellite data and missing satellite data over bright surfaces for the observational based method are also discussed. Further, by using both a global aerosol model and adjustment to an observation-based method, it will in this presentation be demonstrate consistency between the two methods and that the radiative forcing due to the direct aerosol effect is weaker than -0.5 Wm^{-2} .

Secondary organic Aerosol Formation from boreal Tree Emissions

Astrid Kiendler-Scharr, Thomas Mentel, Einhard Kleist, Jürgen Wildt and Andreas Wahner

ICG-2, Forschungszentrum Jülich

A considerable fraction of the organic aerosol component is of secondary origin, meaning it is formed through oxidation of volatile organic compounds (VOCs). Plant emissions, e.g. monoterpenes and sesquiterpenes, are a major source of VOCs in the troposphere. Global models use parameterizations from experiments with single compounds to describe secondary organic aerosol (SOA) formation. In this talk I will present recent studies on the formation and growth of secondary organic aerosol from tree emissions. SOA was formed by ozonolysis and/or photo-oxidation of the VOCs emitted by several tree species such as spruce, pine and birch. The experiments were performed in the Jülich Plant Atmosphere Chamber (JPAC) under well defined conditions for the plant. The SOA was investigated with respect to formed particle number, volume and mass spectral signatures. Our results indicate that the laboratory approach of studying the formation of SOA from single components can lead to a bias in both the formation rates and the mass spectral signatures observed. It was observed that the threshold for SOA formation was lower for the mixture of VOCs emitted from spruce, pine, and birch than for α -pinene as single compound. We therefore conclude that the threshold for SOA formation from real plant mixtures may be much lower than the threshold obtained from laboratory experiments that were focussed on single VOCs. SOA formation from stress induced VOCs will be compared to non stress induced emissions. Possible feedbacks of climate change to VOC emissions and aerosol formation will be discussed based on our experimental observations.

Oxidized Organic Aerosol and Emissions: How do we get there from here?

Neil Donahue

Center for Atmospheric Particle Studies (CAPS)
Carnegie Mellon University, Pittsburgh, PA, USA

Organic aerosol are comprised of thousands of individual organic compounds, many of them as yet unidentified. However, recent ambient data show convincingly that they are typically highly oxidized (OOA) and have relatively low volatility. In contrast, fresh primary emissions are quite volatile and not very oxidized. Even typical lab-generated secondary organic aerosol is also more volatile and less oxidized than ambient OOA. Clearly, quite significant transformations are occurring in the atmosphere beyond those that have been identified in the laboratory so far; a leading candidate is gas-phase oxidation of first-generation semi-volatile vapors by the OH radical. We shall present a two-dimensional framework (volatility basis set -- the 2D-VBS) based on volatility and the oxidation state (O:C) of organic compounds to describe the multi-generational aging of organic vapors associated with OA. Critical unknowns include the relative importance of gas-phase vs heterogeneous and condensed-phase processes as well as the branching ratio between reactions that functionalize organics vs those that fragment the carbon-carbon backbone.

Molecular Characterization of Secondary Organic Aerosol from Isoprene and Monoterpenes

Magda Claeys

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During the past five years considerable progress has been made in our understanding of the fate of the biogenic volatile organic compounds (BVOCs) isoprene and α -pinene (and selected other monoterpenes) in the atmosphere. Secondary organic aerosol (SOA) formation from the oxidation of these BVOCs has been studied in the laboratory with various oxidants (OH, NO₃, and ozone) and under atmospherically relevant conditions, i.e., in the presence of NO_x and sulfuric acid seed aerosol. Molecular characterization of organic aerosol constituents is important because it allows one to gain insights into aerosol sources and the underlying mechanisms of SOA formation and transformation (or aging). An overview will be presented of the current state of knowledge on SOA tracers, which not only can be generated in laboratory smog chamber experiments but are detected at significant concentrations in the ambient atmosphere. A whole range of novel SOA products from the oxidation of isoprene, α -pinene, and 1,8-cineole has been characterized at the molecular level using a suite of analytical techniques such as gas chromatography/mass spectrometry with prior derivatization and liquid chromatography/negative ion electrospray ionization mass spectrometry, and detailed interpretation of the mass spectral data, as well as, in some selected cases, through synthesis of reference compounds. The structural characterization of recently characterized α -pinene SOA tracers has posed a considerable analytical challenge, because they correspond to products where the skeleton of the precursor BVOC molecule is lost and/or they contain unexpected functionalities such as, for example, a lactone group. Interestingly, some of the novel α -pinene SOA tracers were already reported in the early German chemical literature.

Formation of Organosulphates from reactive Uptake of Monoterpene Oxides

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The oxidation of monoterpenes leads to low-vapour-pressure oxidation products that partition between the gas and particle phases. Recent laboratory studies have demonstrated that SOA formation can also occur from the reactive uptake of semi-volatile organic compounds in the presence of acidic sulphate aerosol. HPLC/ESI-MS analysis revealed that these reactions lead to the formation of organosulphates and high molecular weight compounds. Especially, atmospheric relevance of organosulphates is established by field evidence showing the existence of organosulphates and nitrooxy-organosulphates originating from isoprene, α -pinene and β -pinene in ambient SOA. Furthermore, very recent field data suggests that the organosulphates may contribute substantially to ambient SOA.

In the present study, we report the formation of organosulphates from the reactive uptake of α -pinene oxide, β -pinene oxide, campholenic aldehyde and carveol in an aerosol chamber study. SOA samples were analyzed using UPLC/ESI-IMS-QTOFMS (electrospray ionization ion mobility spectrometry quadrupole time-of-flight mass spectrometry). Organosulphates were only detected in the samples from both epoxides and campholenic aldehyde in the presence of acidic sulphate seed particles. In particular, β -pinene oxide yielded much higher concentrations of organosulphate than α -pinene oxide. Campholenic aldehyde and carveol yielded a very little or no organosulphate, indicating that epoxides most likely play an important role in the formation of organosulphates in the atmosphere. This study provides evidence for the reactive uptake of epoxides as a key process leading to the formation of atmospherically relevant organosulphates.

Molecular Simulation of the Surfaces of Aged Sea Salt and Organic Aerosol Particles

Doug Tobias

Department of Chemistry, University of California, Irvine

Heterogeneous chemistry involving tropospheric aerosol particles influences air quality and the role that particles play in determining climate. A full understanding of the kinetics, mechanisms, and consequences of aerosol chemistry requires a molecular picture of structure and dynamics at the air-particle interface that is difficult to obtain by experiment alone. This talk will present a molecular-scale view of heterogeneous processes involving aerosols from the perspective of molecular dynamics simulations, complemented by experiments performed by our collaborators. The specific topics to be discussed are the role of halogen anions in promoting nitrate photochemistry in aged sea salt particles, and the consequences of oxidative processing of organics on the uptake of water.

Photochemistry at Interfaces: the Effect of Light on Trace Gases Uptake

Barbara D'Anna

Université Lyon 1, Lyon, F-69626, France; CNRS, UMR5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, Villeurbanne, France

Earth atmosphere contains aerosol particles characterized by a wide range of sizes (1 nm - 10 μm), aggregate states (solid, liquid, inhomogeneously mixed), and chemical compositions (sea-salt, earth oxides, soot, sulfuric acid, organics, etc.). It is well known that aerosol particles provide a unique heterogeneous environment for atmospheric chemical reactions and have a serious effect on climate and air quality. From a chemical perspective, the key question is the role of chemistry involving aerosol particles in the global atmospheric environment. Can particles catalyze critical reactions in the atmosphere? Another quite intriguing question is how solar radiation can affect the heterogeneous chemistry at the aerosol interface. Indeed UV-A/Visible light absorbing material is largely present in the airborne particles (as soot, mineral oxides, and various organic aerosols as HULIS). Light could therefore promote a “new chemistry” and initiate photocatalytic or photosensitized reactions at the aerosol surface. Few examples of light-enhanced heterogeneous chemistry on soot particles and mineral dust are presented here. Soot was suggested to be an important sink for some atmospheric oxidants (such as O_3 or NO_x) and as consequence, its heterogeneous chemistry has been largely investigated in the past years. However, its atmospheric impact appeared to be quite limited due to a rapid soot surface passivation. As previous studies were done under dark conditions, we decided to investigate the effect of light on the uptake kinetics of NO_2 on soot. The results showed that the NO_2 uptake on soot is considerably enhanced under irradiation leading to NO and HONO production. Uptake coefficients increased both with soot mass and the irradiation intensity. The importance of soot photochemistry will be presented and discussed as our results suggest that photo-induced uptake may be important under atmospheric conditions. Another important class of aerosol is represented by mineral dust aerosol. Evidence from field, laboratory and modelling efforts are increasingly pointing towards an important role of mineral dust as provider of reactive surfaces for several trace gases. The interaction of mineral dust with atmospheric NO_x – NO_y trace gases is particularly interesting due to its potential impact on photochemical ozone production. And an increase in the nitrate content of dust during transport over polluted regions has been documented on several occasions and model studies have confirmed that this is consistent with the uptake of reactive NO_y traces gases. Nitrate formation on dust particles is therefore considered a sink for atmospheric NO_y (such as HNO_3). This work shows that mineral dust is an effective photocatalyst (due to Ti, Al and Fe traces) which catalyze NO_2 conversion into HONO and nitrate ions on mineral dust and proxy (SiO_2 - TiO_2) under near-UV irradiation. In addition to NO_2 conversion, the photoinduced loss of other important traces gases as O_3 and formaldehyde at the surface of the minerals oxides (SiO_2 - TiO_2) is demonstrated. Considering the photocatalytic properties of mineral dust, the stability of nitration anions on dust and the possibility of a “renoxification” process, with NO or NO_2 production, has also been investigated. We further present results of photodissociation of nitrate ion doped mineral oxides such as SiO_2 and/or TiO_2 at mixing ratios related to atmospheric issues.

Atmospheric chemistry at aqueous surfaces: what have we learned and where are we going?

D. J. Donaldson

Department of Chemistry, University of Toronto

It has been less than a decade since the first reports of direct measurements of atmospheric reactions taking place at the air-aqueous interface. In that time, many reactions of ozone at the surface have been quantified, as well as a tiny number of other systems. I will discuss several of our studies which probe the interfacial kinetics and suggest some new avenues for exploration in the future.

Hydrolysis reactions take place in the near-interface region, although not exactly at the top of the water surface. In the dark, the reactions of ozone at the liquid (and solid) water surface all seem to follow a Langmuir-Hinshelwood kinetic mechanism; on the ice surface, the kinetics appear to be much more rapid than at the liquid surface. Photoredox reactions at the air-aqueous interface could be an important source for halogenated species and nitrogen oxides into the boundary layer.

Atmospheric Chemistry at Air-Water Interfaces

Michael R. Hoffmann

Engineering & Applied Science, California Institute of Technology

We have studied a wide range of droplet phase chemical reactions involving the ozone in the gas-phase reacting with chemical substrates the droplet interface. These reactions are studied using sonic electro-spray mass spectrometry. In addition, we have studied the interfacial partitioning of anions to droplet interfaces using this approach. The underlying principles will be highlighted and specific examples presented such as the anion-catalyzed disproportionation of NO₂ to produce HNO₃ and HONO, the oxidation of Br⁻, I⁻ and Cl⁻ ions by O₃, the oxidation of organics by ozone, and the photolysis of low-molecular weight keto-carbonyl compounds to produce self-assembling oligomeric clusters.

Some Details

The reactive dissolution of NO₂(g) on cloud and fog droplets and the conversion to HONO(g) : $2 \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) = \text{HONO}(\text{g}) + \text{NO}_3^-(\text{aq}) + \text{H}^+(\text{aq})$, is a viable transformation process. Recently, unexpectedly large HONO concentrations were observed that may account for ~ 50 % of OH radical production at noon and entail a diurnal source ~ 64 times stronger than the reaction above at night (Kleffmann, *Chem. Phys. Chem.* **2007**, *8*, 1137). Reported NO₂(g) uptake coefficients in water are at odds in the range from $\gamma < 10^{-7}$ up to 10^{-3} . Here we show that the probability of NO₂ uptake on aqueous microdroplets depends on their ionic composition at the air/water interface, reaching peak values at ion concentrations in the low mM range, using a novel application of electrospray mass spectrometry. We found that the uptake rates under these conditions are three orders of magnitude larger than in pure water. Uptake appears to be controlled by the capture of NO₂ into radical anion intermediates on droplet surfaces, and is modulated by overall anion concentration. These results would resolve the outstanding discrepancies between previous NO₂ uptake measurements in water vs. NaCl-seeded clouds, and lead to half-lives for the reactive dissolution of NO₂ in typical clouds and fogs that are sufficiently short to impact diurnal ·OH/HO₂· budgets.

The refractory, water-bound perfluoro-*n*-alkyl carboxylate (*n*-PFC-) and sulfonate (*n*-PFS-) surfactants reach remote locations hydrologically unconnected to their sources via hitherto unknown processes. Here we quantify the enrichment of these anions in microdroplets produced by aerosolization of 1 μM aqueous surfactant solutions at pH 7 using sonic spray ionization mass spectrometry. Relative enrichment factors *f* steeply increase from *n* = 1 to 3, level off at $f(\text{n-PFS-}) \sim 2.3 f(\text{n-PFC-}) \sim 190 f(\text{Br-})$ (*n* ≥ 8), and display even-odd effects. The preferential enrichment of *n*-PFS- over *n*-PFC- reflects a larger headgroup. The hyperbolic, rather than the predicted linear ln *f* vs. *n* dependence suggests the onset of conformational restrictions to interfacial enrichment above *n* ~ 3. Marine aerosols produced from contaminated ocean surface waters are thus expected to be highly enriched in PFC-s/PFS-s. The monotonic accumulation of 8-PFS- and PFC-s in East and, less pronouncedly, in West Greenland biomarkers is therefore consistent with the deposition of marine aerosol drawn from contaminated North American Current waters and transported westward by predominant easterlies. The analogous trend for PFC-s in Canadian Arctic biota vis-a-vis the rapid decline of 8-PFS- after 2000 suggest that the fresher Labrador Sea does not sustain a similar process over this region.

Humic substances (HUMICS) are widespread in natural surface waters, where they ultimately undergo solar photolysis into small alpha-dicarbonylic species, such as glyoxal, glyoxylic and pyruvic acids. Humic-like substances (HULIS) are also found in the atmospheric aerosol. We

report a laboratory study of the photolysis of aqueous pyruvic acid (PA), solutions at concentrations representative of the atmospheric aerosol using UV-absorption, high resolution electrospray mass (EMS), and nuclear magnetic resonance (NMR) spectrometries. PA yields polyfunctional oligomers reaching molecular masses of up to 900 Da, some of which absorb into the visible. Exact mass determinations (to the fourth decimal place) yielded unique molecular formulae in most cases, which were confirmed by collisionally induced dissociation (CID) patterns and the analysis of the products of photolysis of [2-¹³C] and [3-¹³C] PA isotopologues. The lowest energy CID channels corresponded to neutral fragment losses of masses: 18 (H₂O), 44 (CO₂), 46 (HCOOH) and 62 (CO₃H₂). ¹³C- and ¹H- NMR of [2-¹³C] and [3-¹³C] PA photolysis mixtures revealed the presence of various carbonyl functionalities (190 to 230 ppm) displaying ²J(CC) and ³J(CC) couplings among themselves and with anomeric carbons (~ 96 ppm). Based on this evidence, we propose molecular structures and a mechanism of formation for these oligomers.

Biosurfaces are universally covered with fluid microfilms containing reduced glutathione (GSH) and other antioxidants whose putative roles include the detoxification of ambient ozone (O₃). It is generally believed that O₃ accepts an electron from the thiolate GS²⁻ function [pK_a(GS⁻) 8.8] of GSH to produce thiyl GS• radicals en route to the disulfide GSSG. Here, we report novel electrospray mass spectrometry experiments showing that sulfonates (GSO₃⁻/GSO₃²⁻), not GSSG, are the exclusive final products on the surface of aqueous GSH microdroplets exposed to dilute O₃(g) for 1 ms. The higher reactivity of the thiolate GS₂⁻ toward O₃(g) over the thiol GS⁻ is kinetically resolved in this time frame due to slow GS⁻ acid dissociation. However, our experiments also show that O₃ will be largely scavenged by the more reactive ascorbate co-antioxidant in typical interfacial biofilms. The presence of GSSG and the absence of GSO₃⁻/GSO₃²⁻ in extracellular lining fluids are therefore evidence of GSH oxidation by species other than O₃.

Could Micro-organisms play an active Role in Atmospheric Chemistry ?

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During the last years, a lot of research papers dealing with aerobiology have been focused on pollens and vegetal or animal debris. However, the organic fraction also includes micro-organisms like viruses, bacteria and fungi that are found among the biological atmospheric particles. They are present in indoor air, in the troposphere and even in the stratosphere but our knowledge on their global distributions and on their importance in atmospheric physical and chemical processes are still very limited. It should be stressed that the majority of the papers only reports a description of the microbial population found in the air but recent studies show that living micro-organisms are also present in the atmospheric water phase including snow, fog and clouds.

This talk is focussed on micro-organisms present in clouds since we believe that studying micro-organisms in the water phase of the atmosphere is the most relevant to understand their potential role in atmospheric chemistry (and also microphysics). First, the life cycle of micro-organisms will be examined *via* the atmosphere from their aerosolisation to their integration in clouds and their return to the Earth by precipitation. Then, a short description of micro-organisms in clouds will be given including some specific characters that allow them to be in clouds and their variability in numbers and nature depending on the air mass origin and seasons. Indeed, the viability and metabolic activity of airborne micro-organisms depend strongly on physical and chemical atmospheric parameters such as temperature, pressure, radiation, pH value and nutrient concentrations. The third section will be devoted to their potential role as biocatalysts transforming organic compounds in clouds and a discussion about microbiology as an alternative route to photochemistry.

Since our knowledge of the microbiological and chemical interactions of micro-organisms in the atmosphere is rather limited, further targeted investigations combining laboratory experiments, field measurements, and modelling studies will be required to characterize microbiological activities and will be described in this talk.

Incoherent Broad-Band Cavity-enhanced Spectroscopy for atmospheric Studies

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Cavity-enhanced absorption spectroscopy (CEAS) is a promising technique for atmospheric studies due to the very long optical paths while keeping the sampled volumes rather small. Incoherent broad-band (IBB) light sources can be used readily for CEAS as long as sensitive detectors are available. In this talk we show some applications of IBB-CEAS for the atmospheric detection of radicals and trace species like NO₃, HONO, NO₂, IO, OIO, I₂ using their electronic bands in the ultraviolet-visible, and first high-resolution laboratory measurements in the near-infrared region using a Fourier-transform spectrometer (FT-IBB-CEAS).

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High Resolution PTR-TOF A New Instrument for Organic Compound Measurements

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Over the last decade proton transfer reaction mass spectrometry (PTR-MS) has become very popular in many scientific fields. PTR-MS allows for the quantitative detection of volatile organic compounds (VOCs) at pptv level virtually in real time. Monitoring of VOCs with a time resolution of typically a second per compound has, for instance, enabled the tracking of pollution plumes by air-borne measurements, thus revealing the photo-chemical fate of pollutants. This rapidity, however, has been achieved at the cost of the number of compounds to be analyzed and compound selectivity. Conventional PTR-MS can, for example, not distinguish between isobaric species, e.g. between glyoxal and acetone.

The use of a time of flight (TOF) instead of a quadrupole mass analyzer in PTR-MS provides a sufficient high mass resolution to identify the atomic composition of product ions by their exact mass and their characteristic isotope patterns. In addition PTR-TOF can record full mass spectra within a fraction of a second which is a dramatic increase in duty cycle. At the University of Innsbruck a high resolution PTR-TOF has recently been developed, coupling a PTR ion source and a high resolution TOF. We achieved a mass resolving power of 6000 (FWHM), and a detection limit of tens to a few hundreds of pptv if integrating mass spectra for one minute.

First results from a series of 1,3,5-trimethylbenzene (TMB) photo-oxidation experiments performed under various NO_x conditions in the 27 m³ Paul Scherrer Institute environmental chamber will be presented. Using the PTR-TOF, more than 300 VOCs were found during TMB photo-oxidation experiments and corresponding time traces were recorded. About 100 VOCs were present with volume mixing ratios > 0.5 ppbv. Empirical formulas C_nH_mN_pO_o were determined and VOCs were separated and grouped according to their C, O and N numbers. This allowed determining photo-oxidation grade dependent values such as the O / C ratio and time traces of mono- and multi-oxygenated compounds. The results are compared with results predicted by the Master Chemical Mechanism (MCM).

Acknowledgments:

The TOF-MS system was funded by the University of Innsbruck („Uni Infrastruktur 2004“ Programme). The PTR-TOF was developed in collaboration with Ionicon Analytik GmbH and with assistance from TOFWERK AG. The development project is financially supported by the Austrian Research Funding Association (FFG; project 810074). The smog-chamber experiments were financially supported by the ESF-programme INTROP, and EUROCHAMP.

On-line Aerosol Measurements – Results from Recent Field Campaigns

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An overview of results from a variety of field measurement campaigns of aerosol parameters at very different locations is given. On-line measurements of aerosol and partially trace gas parameters were performed at sampling sites ranging from remote and clean environments, like the Southern Atlantic Ocean, over coastal sites up to urban environments and immediate surroundings of industrial plants. Thus, these measurements cover almost the whole accessible spectrum of pollution, often reaching the limits of the measurement equipment at one or the other end.

In order to perform successful aerosol measurements under such diverse conditions, development and characterization of instruments, data processing algorithms and sampling platforms has been done. This includes the characterization and optimization of an aerosol mass spectrometer and further enhancement of data processing algorithms for this instrument, as well as, the development of the Mobile Laboratory (MoLa) for aerosol research.

During the OOMPH (*Organics over the Ocean Modifying Particles in both Hemispheres*) campaign, an Aerodyne Aerosol Mass Spectrometer was used to characterize the submicron aerosol in the Southern Atlantic Ocean. Results from these measurements show clear differences in the aerosol characteristics found in different air masses encountered during this cruise. Using a new data processing approach, it was possible to differentiate methane sulfonic acid (MSA) from other organic aerosol components on a physical basis for the first time. Also, during the DOMINO (*Diel Oxidant Mechanisms In relation to Nitrogen Oxides*) campaign, it was possible to investigate aerosols from continental and marine origins, and in addition urban influenced aerosol. This measurement campaign took place during a three week period in the Mediterranean winter at the Spanish Atlantic coast. Here, a large variety of aerosol parameters including particle number and mass concentration, particle size distributions, and particle chemical composition was determined. In addition, trace gas concentrations and meteorological parameters were measured, providing a broad picture of atmospheric conditions.

During the trip from Mainz to southern Spain and back, the recently developed Mobile Laboratory (MoLa) was employed to collect ambient aerosol data. This resulted in a 5200 km long track of ambient aerosol and trace gas characteristics through Western and Southwestern Europe. Aerosol number concentrations and size distributions were determined, as well as, the chemical composition of the submicron aerosol, providing again – together with the trace gas data – a wide variety of information on the atmospheric composition in several areas in this part of Europe, including major urban agglomerations like Paris, Bordeaux, and Madrid.

Finally, aerosol concentration and size distribution measurements, as well as, aerosol composition measurements were performed in the vicinity of an integrated steel plant, next to a coke oven facility, and in the exhaust train of a waste incinerator. Here, highly temporally resolved aerosol data were collected, allowing improved source apportionment and process studies.

These aerosol studies at such different locations and under such a variety of conditions provide an overview of both, the capabilities, and also the limitations of current modern aerosol measurement instrumentation.

A Superposition of Microphysics and Absorption Effects of Aerosol on Clouds

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There are two main “channels” in which aerosol can change cloud properties; the microphysical and the radiative channels. Aerosol, serving as cloud condensation nuclei, changes the size distribution of the cloud droplets and therefore can change condensation/evaporation rates, latent heat release, collision coalescence efficiency, cloud dynamics and all the derived cloud properties such as reflectance, lifetime, phase, size, and precipitation. On the other hand absorbing aerosol can change the atmospheric profile by heating the aerosol layer and cooling the layers below. This may stabilize shallow layers and choke shallow clouds in or below the aerosol layer and destabilize the profile above the aerosol layer.

The overall effects on the redistribution of radiative and thermodynamic energy depend on the type and size of clouds, the atmospheric profile and the aerosol properties.

Aerosol Remote Sensing: Principles, Evolution and Perspectives

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Atmospheric aerosols affect the radiative budget of atmosphere directly by scattering, absorbing and reflecting incoming solar radiation back to space or indirectly by changing distribution and properties of clouds. Overall, the aerosol climate forcing tends to partly offset the global warming impacts associated with greenhouse gases. However, the aerosol lifetime is much shorter than that of most greenhouse gases and the aerosol concentration varies strongly with space, so the aerosol climate impact cannot be treated as a mirror image of global warming. This high time and spatial variability of aerosol also makes the detection and characterization of aerosol properties highly challenging. Due to both difficulties of characterization and complexity of the mechanisms of aerosol climate interactions, the uncertainty in quantifying aerosol effects on the climate has been recognized as a main uncertainty in the estimating anthropogenic forcing of climate. In addition to climate change, emitted gases and aerosols create air pollution directly resulting in health effects for humans, damaging effect on flora and fauna, and causing acid rain. It is usually related to the large-scale fossil fuel combustion and fossil fuel related activities, as well as, biomass burning and changes in land use. Aerosols, or microscopic particles in the air, can cause respiratory ailments, reduce visibility and damage buildings. Due to importance of these anthropogenically generated effects, during several last decades significant efforts were undertaken for characterizing distribution and properties of aerosols resulted in significant developments of diverse observations, modelling and characterization tools.

Remote sensing is probably the most adequate observational approach for characterizing properties of atmospheric aerosol required for accounting for aerosol effect in climatic studies. Indeed, the satellite remote sensing is unique technique for monitoring time variability of the aerosol at regional and global scales. Compare to *in situ* and laboratory measurements, remote methods do not use aerosol sampling and allow accessing the properties of unperturbed ambient aerosol in the atmospheres. In addition most of remote sensing methods use the ability of aerosol particles to interact strongly with electromagnetic radiation. The same ability makes aerosol one of most climatically important atmospheric component. Therefore, the remote observations have high sensitivity to the variations of aerosol properties that most needed for the climatic analysis.

The purpose of this presentation is to outline the main principles used in remote sensing and discuss evolution, current state and future perspectives of the satellite and ground-based remote observations obtained by both passive and active optical measurement techniques. In addition, the ongoing efforts to overcome limitations of aerosol remote sensing by means of synergizing remote methods with other approaches of aerosol characterizations, such as, *in situ* analysis and chemical aerosol modeling will be discussed.

Global Modeling: Applications at the Joint Research Centre

Frank Dentener and Elina Marmer

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The research at the Climate Change Unit of the Joint Research Centre in Ispra, Italy is dedicated to provide scientific background to European policies on air pollution and climate change.

Implementation of policies requires knowledge on the contribution of certain source categories, source regions and components to observed levels of air pollution.

We employ the global 3D two-way nested zoom chemistry transport model TM5 zooming on respective regions of interest:

In the Mediterranean region, we focus on the impact of ship emissions on the air pollution. Ship emission inventories largely differ from one another due to different methodologies, ship activity data and emission factors. We apply three different ship emission inventories in TM5 and evaluate the results with onboard ship measurements and satellite retrievals.

In India and China, we are investigating the impact of emission reduction policy on province and state levels on the surrounding regions within the framework of GAINS Asia.

For the HTAP (Hemispheric Transport of Air Pollution) activity, we zoom our model on four world regions simultaneously - Europe, North America, East Asia and South Asia. The multi-model comparison within the SR (source-receptor) experiment is aimed to identify to what extent perturbing emissions in one world region affects pollution levels in others.

The interactions between air pollution and climate are investigated utilizing the TM5 model, the radiation transfer model ORTM and the global aerosol climate model ECHAM5-HAM. We analyze the benefits and trade-offs of climate policy and air pollution reduction scenarios on regional and global scales and assess their impacts on climate and human health.

Feedbacks between Aerocol Cycles and Climate

Johann Feichter

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The Earth's climate is controlled by numerous factors. These include oceanic, terrestrial and anthropogenic emissions of trace gases and aerosol particles. The climate system reacts directly to a forcing and indirectly through numerous interactions and feedbacks between the components. To estimate sign and magnitude of these feedbacks is one of the most challenging issues in climate system research.

Aerosol particles influence climate relevant processes of the atmosphere, ocean and biosphere, and thus the exchange between the different Earth System components. There is a strong coupling between changes of the surface energy budget, due to greenhouse gas warming and aerosol cooling, and precipitation as well as between aerosol concentrations, clouds and precipitation processes. In the atmosphere aerosol particles from the biosphere and anthroposphere act as cloud condensation nuclei and ice nuclei and modify the micro-physical properties of clouds, with potential consequences for cloud macro-physical properties. In the ocean the deposition of iron containing mineral dust advected from land deserts may play a role in controlling the marine primary productivity. In return, environmental properties influence the properties of aerosols. For example, the production and atmospheric release of gaseous and particulate matter from natural sources as for instance DMS from marine biosphere, VOC from vegetation, mineral dust and sea-salt, is largely controlled by temperature, precipitation and surface winds. All these interactions and feedbacks demonstrate the important role of particulate matter in the climate system and the need for complex Earth-System models to investigate properly the role of aerosols.

EUROCHAMP-2: Atmospheric Simulation Chambers for Studying Atmospheric Chemical Processes

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Laboratory studies allow one to obtain detailed information about chemical reactions under well defined conditions (p,T). An important approach to better understand the complex chemical processes in the atmosphere are so-called atmospheric simulation chambers (smog chambers), which sometimes have a volume of several hundred cubic meters. Smog chambers allow the simulation of quite different atmospheric conditions without the complication of transport processes. The general objectives of the EU funded infrastructure project EUPHORE which started in June 1, 2004 and had a duration of 60 months were:

- The integration of existing environmental reaction chambers into a Europe-wide infrastructure
- Initiation of an effective interdisciplinary collaboration between the community of atmospheric scientist and colleagues from other disciplines (cultural heritage protection and human health)

EUROCHAMP had three networking activities, 1. protocols for raw data analysis, data intercomparison and quality assurance, 2. central database of environmental chamber studies and central spectroscopic database, and 3. meetings and infrastructure-related workshops. It also had two joint research activities (JRAs):

JRA1: development and refinement of experimental techniques (for oxygenated VOC's, for inorganic trace gases and radicals, for surface reactions in chambers etc)

JRA2: development of common techniques for the use of chamber measurements in model development and evaluation (techniques for the evaluation and development of oxidant mechanisms and models, techniques for the evaluation and development of aerosol models, development and deployment of statistical tests and sensitivity analysis methods)

The activities within EUROCHAMP proved to be very successful and attracted international acclaim. The success of EUROCHAMP has led to the funding of EUROCHAMP-2 which will start on May 1, 2009, has 14 partners and a duration of 48 months. EUROCHAMP-2 will have the same salient features as EUROCHAMP, however, the activities within the work packages have been considerably extended. In addition, there will be an activity called Transnational Access (TNA). The TNA will provide users outside the consortium with financial support to use the EUROCHAMP-2 chambers. For selected proposals the support will include travel and accommodation, and operational costs for the EUROCHAMP-2 installation to be used.

The talk will describe the major aspects of the EUROCHAMP-2 project.

Atmospheric Degradation of Amines – Results from a Screening Study

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Technology based on amines is close to being operational in industrial post-combustion CO₂ capture. In operation a plant will eventually leak amines to the environment. Maximum emission of amine from a single plant capable of capturing 1 Mt CO₂ per year is expected to range from 40-160 tonnes per year. There are currently no regulations in Norway regarding permissible levels of exposure via air and drinking water for amines and other potential problematic compounds that could be formed in the atmospheric oxidation of amines released from CO₂ capture plants.

Chemical reactions in the gas phase are considered the main removal pathway of most volatile organic chemicals in the atmosphere: the atmospheric lifetime for the investigated amines with respect to reaction with OH radicals is only a few hours. Other removal pathways are wet and dry deposition, and photolysis. Theoretical reaction pathways of amines in the gas phase (photo-oxidation schemes) have been constructed on the basis of well established reaction mechanisms for alkanes and oxygenates and existing information from laboratory studies of simple amines.

Results and conclusions from studies of 2-aminoethanol, 2-amino-2-methyl-1-Propanol, 2,2'-(methylimino)bis-Ethanol, and piperazine will be presented. The stable compounds formed from atmospheric degradation of these amines include different amides and aldehydes, but a number of *N*-nitrosamines, *N*-nitramines and *N*-nitroamides may also result. Ongoing risk assessment studies on amines require an accurate determination of the relative amounts of toxic compounds formed in the atmospheric degradation of amines. The only certain way to assess these is the experimental investigation of the compounds in an atmospheric reaction chamber. Preliminary results from recent experiments will be presented.

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POSTER ABSTRACTS

Kinetics of Chlorine-Initiated Oxidation Reactions of Aldehydes

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Aldehydes (RCHO) are important trace constituents of the atmosphere. They have both natural and anthropogenic sources, with small primary sources associated with vehicle exhaust and industrial activity and larger secondary sources associated to the degradation of volatile organic compounds. In the troposphere, abstraction of the aldehydic H-atom by OH radicals leads to acyl radicals RC(O), which combine with oxygen to give acylperoxy radicals RC(O)O₂. The chemistry of acylperoxy radicals has been largely studied these last years. They have several important roles in atmospheric chemistry, and they notably react rapidly with NO to give NO₂, which will lead to ozone formation when photolysed. RC(O)O₂ radicals react also with NO₂ to form stable peroxyacylnitrates RCOO₂NO₂. In air masses with low NO_x concentration, acylperoxy radicals undergo reactions with HO₂ and other peroxy radicals. Reactions of acylperoxy radicals with HO₂ radicals may be important as a source of ozone and carboxylic acids in the atmosphere.

In this presentation will be shown recent experimental and theoretical developments on reactions of Cl atoms with aldehydes (Cl being often used as a suitable laboratory source of RC(O)O₂ radicals).

Correlation among Combustion Effluent Species in an Urban Air Basin

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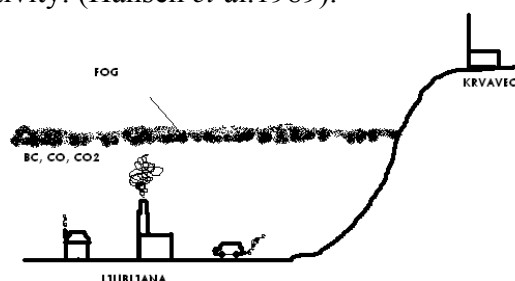
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Keywords: BC, CO₂, diesel exhaust, air pollution, emission factor

Ljubljana is the capital city of Slovenia with approximately 300,000 inhabitants. It is situated in a basin, with frequent temperature inversions during the winter. The urban atmosphere is impacted by traffic during rush hour (250,000 cars/day), two power plants burning gas and coal, and other human activities.

In mid-winter 2008, we measured aerosol black carbon (BC) and carbon dioxide (CO₂) using an Aethalometer[®] (Portable Model AE42, Magee Scientific) and CO₂ sensor (GMP343 Carbon Dioxide Probe, Vaisala). Measurements were made at the Observatory Yard of the Environment Agency of the Republic of Slovenia (EARS) within the city, and at a regional background EMEP/GAW Station on Mt. Krvavec (29 km. distant, 1740 m. altitude).

The major effluent species from combustion are carbon dioxide (CO₂) and water vapor. Minor species emitted include gases such as sulphur dioxide, nitrogen oxides, methane and other organics, and aerosol particles. These contain substantial concentrations of graphitic or black carbon (BC) which can only be produced by incomplete combustion of carbonaceous fuels. The emission of minor species during combustion is governed strongly by the nature of fuel, the efficiency of combustion, and the extent and efficacy of emission controls. The relation between CO₂ and BC represents the emission index for a source: if these species are correlated in ambient measurements, we can estimate an overall BC emission index for the composite combustion activity. (Hansen *et al.* 1989).



Figures 1 and 2 show the results of measurements in January 2008. The good correlation between pollutants indicates a commonality of emission sources. Meteorological influence is strong: episodes of high concentration correlate well with conditions of stagnation and/or temperature inversion.

Table 1: CO₂/BC ratio during several episodes

Episode	k	R ² (BC/CO ₂)
1	0,0078	0,489
2	0,0043	0,794
3	0,0062	0,661
4	0,0049	0,879
5	0,0008	0,061
6	0,0047	0,872
7	0,0034	0,374

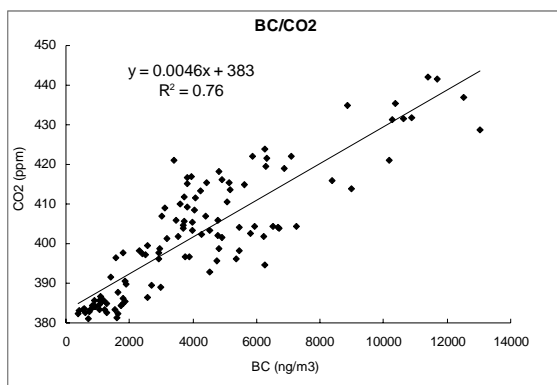


Fig. 1: Scatter plot of CO₂ versus aerosol BC

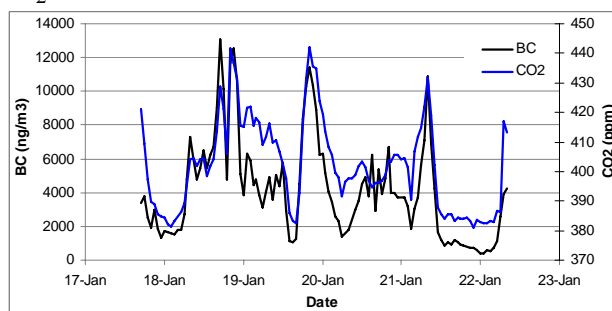


Figure 2: Time series of BC and CO₂ concentrations during one week in winter 2008.

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Emissions of Trace Gases and Aerosols from Prescribed Fires in Portugal

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Summer heat-waves in southern Europe have become more frequent and are expected to increase in frequency and harshness in association with projected global warming thus originating more severe forest and bush fires. Globally, wildfires release billions of tonnes of carbon into the atmosphere that, in turn, accelerate warming even further. Besides emission inventories, climate change, atmospheric photochemical and source apportionment models also use emission profiles which should reflect the regional characteristics of biofuels. However, considerable uncertainties remain regarding the magnitude of carbon exchanges between the wildland fires and the atmosphere. Observational data in this area are scarce and mostly focused on tropical forest and savannah burning.

Several organic and inorganic compounds both in the gas and particle phase were measured in the emissions of controlled burnings carried out in May 2008 at a shrub-dominated forest with some pine trees in Lousã Mountain, central Portugal. From the Fourier transform infrared spectrometry gas measurements, an average modified combustion efficiency of 0.97 was obtained, undoubtedly suggesting a preponderance of flaming combustion. Emission factors were determined for the various gaseous constituents and compared with those published for tropical forest and savannah biomass burning. It was observed that emission factors were generally lower than those published for fires in other regions of the Globe. The organic (OC) and elemental carbon (EC) in fine (PM_{2.5}) and coarse (PM_{2.5-10}) mode particles were analysed by a thermal-optical technique. Approximately 60% of the particulate mass was carbonaceous in nature with a clear dominance of organic carbon. The OC/EC ratios up to 300, or even higher, measured in the present study largely exceed those obtained by other researchers. The water soluble ions and metals in aerosols were quantified by ion chromatography and instrumental neutron activation analysis, respectively. More than 30 trace elements and ions have been determined in smoke aerosols, representing in total an average contribution of about 7% to the PM₁₀ mass. In addition, aerosols were subjected to detailed organic characterisation by gas chromatography-mass spectrometry. Sugars and polyols were quantified by high performance anion exchange chromatography with electrochemical detection. Cellulose was analysed by photometry after its enzymatic conversion to cellulose. The organic compound fingerprint of the particulate matter enabled the quantification of several molecular tracers (e.g. amyryn and syringyl derivatives, anhydrosugars, etc.) for the combustion of Mediterranean forest ecosystems, which could be conducive to source apportionment studies.

Atmospheric Aging of Pesticides: Heterogeneous Reaction of Cypermethrin with Ozone and UV radiation

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Pesticides are highly toxic compounds that unlike other pollutants are intentionally introduced, in large quantities, to the environment. The vast majority of them are applied to agricultural lands, but they are also widely used in urban areas as herbicides, insecticides and fungicides. Pesticides may be promoted into the atmosphere during their application via drift of aerosols, as well as by volatilization or dust erosion from treated surfaces after application. In the atmosphere, semi-volatile pesticides may remain as pure aerosols or become adsorbed upon background aerosols. During transport, they undergo chemical degradation processes due to their interaction with atmospheric oxidants or solar radiation. Quantification of the reaction rate constants and degradation products will allow for better risk assessment and environmental fate evaluation of these hazardous materials. Here, we focus on the investigation of the heterogeneous oxidation reaction of cypermethrin, a common used insecticide, with gaseous ozone and UV radiation. The reactions are monitored in real time using novel apparatus that combines ATR/FTIR and Long path IR gas cell for simultaneous monitoring of the condensed and gas phases. The environmental implication of the observed kinetics and degradation products are also discussed.

The Gas Phase Ozonolysis of β -Pinene

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The reaction rate and primary product distribution of the O_3 -initiated oxidation of β -pinene were characterized using transition state theory and statistical kinetic RRKM/Master Equation analyses, based on DFT, CBS-QB3 and CASPT2 quantum chemical calculations. The predicted rate coefficient of the initial O_3 attack on the exocyclic double bond shows a slight positive temperature dependence, $k_{tot}(T) = 1.27 \times 10^{-22} \times T^{2.64} \times \exp(-714 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and is in close agreement with experiment. The resulting primary ozonides are found to give rise to two distinct, non-interconvertible conformers of the predominant Criegee Intermediate (CI-1 and CI-2), with subsequent chemistries that are shown to be very different; this crucial aspect of β -pinene ozonolysis was not taken into account in an earlier theoretical study by Zhang and Zhang. One of the CI conformers, CI-2, carries nearly half the total reaction flux, and cannot undergo the usual "hydroperoxide channel", thus rationalizing why the OH yield from β -pinene is roughly half that from α -pinene.

The predicted first-generation product distribution for atmospheric conditions is consistent with the available experimental data on the overall products. Our final results predict 5% of nopinone formation, 28% OH radicals with 2-oxo-alkyl radical coproducts, 37% of stabilized Criegee intermediates (SCI), 17% lactones, 10% CO_2 formed after an intersystem crossing, and 3% of a newly proposed biradical formed from prompt ring opening in the CI.

The secondary chemistry of the high-mass reactive intermediates is also examined for atmospheric conditions. Stabilized Criegee intermediate CI-1 is expected to yield additional OH production via the thermal unimolecular "hydroperoxide channel". The reaction of stabilized CI-2 with H_2O and its dimer is expected to outrun the "dioxirane channel", to produce some additional nopinone. The fate of the 2-oxo-alkyl radical coproducts of OH formation is summarized, as well as the chemistry of the singlet biradical. The chemistry of these intermediates will depend strongly on the reaction conditions, i.e. the relative concentrations of HO_2 , RO_2 , and NO coreactants.

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Analytical Developments, Reactivity and Toxicity of Polycyclic Aromatic Compounds associated to Atmospheric Particles

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Polycyclic Aromatic Hydrocarbons (PAH) and their derivatives are ubiquitous organic compounds widely found in all environmental compartments. In the atmosphere, they are mainly emitted as by-products of organic matter and fossil fuel incomplete combustion such as domestic heating, automobile fuel combustion, wood burning and other industrial processes. For the most part, atmospheric PAHs have an anthropogenic origin. Once emitted in the atmosphere, PAHs are present both in gaseous form and adsorbed onto particles, depending on their volatility. The main concern of PAHs is that some of them are reported to have carcinogenic and mutagenic properties. Once emitted into the atmosphere, they may be submitted to photodegradation and/or chemical oxidation (O_3 , OH, NO_x ...). Many studies show that the oxidation products formed in such processes (nitro-PAHs, oxy-PAHs...) are often more toxic than parent compounds.

Last results dealing with the global study of PAHs in the atmosphere will be presented, including: analytical developments, presence and fate, their heterogeneous reactivity with OH, NO_2 and O_3 , and mutagenicity assessment.

Uncertain Atmospheric Chemistry in Urban Air: Oxidant Fields, and Aerosol Optical Properties

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In the high NO_x chemical regime - typical for urban areas - the observed levels of OH and HO₂ radicals are inconsistent with our current understanding of HO_x chemical cycles. Experimental testing of atmospheric models to predict oxidant fields in Mexico City (Volkamer et al., 2007a; Sheehy et al., 2008) reveals considerable shortcomings in the knowledge base that underlies current chemistry modules (gas- and aerosol phase) that are important for predicting the formation of secondary pollutants that form as a result of chemical transformations in the atmosphere, i.e., ozone and secondary organic aerosol (SOA). In this poster we consider recent laboratory and field evidence for novel radical sources (Li et al., 2008; Osthoff et al., 2008; Roberts et al., 2009) and radical recycling routes (Buskovskaya et al., 2007; Cariolle et al., 2008) in terms of their potential to help explain uncertain radical budgets in Mexico City. The recent realization that most organic aerosol (OA) forms as SOA emphasizes the need to accurately predict oxidant fields in order to make meaningful predictions of fine particulate mass, which adversely affects human health, and cools our climate by scattering incoming solar radiation back to space. Glyoxal (CHOCHO) uptake to particles is an important building block for SOA in Mexico City (Volkamer et al., 2006; Volkamer et al., 2007b) and on global scales (Fu et al., 2008; Myriokefalitakis et al., 2008). Recent laboratory evidence shows that SOA from CHOCHO alters the optical properties of OA (Shapiro et al., 2009) consistent with recent our field evidence that OA absorbs incoming solar radiation much stronger than currently believed in Mexico City (Barnard et al., 2008). Here we assess how uncertain assumptions about OA optical properties affect satellite retrievals of trace gases over aerosol hot spots. We identify a strong coupling between OA optical properties and the column abundances of trace-gases as visible from space that is currently not being considered with attempts to infer emission trends by monitoring certain indicator gases from satellite. The atmospheric chemistry controlling oxidant fields and SOA formation is uncertain, and in addition to uncertain meteorology and emissions, this chemical uncertainty needs to be considered to infer emissions from space, and manage air quality and climate effectively.

Direct Observations of Reactive Trace Gases over the Tropical Pacific Ocean: Field Evidence for Novel Chemistry at the Ocean Atmosphere Interface

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A novel Ship Multi AXis DOAS (CU SMAX-DOAS) instrument, developed at CU Boulder's Atmospheric Trace Molecule Spectroscopy Laboratory (AMTOSpeclab), was deployed from October 2008 to January 2009 on board NOAA's RV *Ronald H. Brown* over the Eastern Pacific Ocean to directly probe the column abundance of glyoxal (CHOCHO), iodine oxide (IO), iodine (I₂), iodine dioxide (OIO), bromine oxide (BrO), nitrogen dioxide (NO₂), nitrous acid (HONO), formaldehyde (HCHO), sulfur dioxide (SO₂), water vapor (H₂O) and oxygen dimers (O₄, an indicator for aerosol optical depth) as part of the VOCALS-REx and TAO field campaigns. Different satellites disagree as to the abundance of CHOCHO over the oceans. It is further not clear whether CHOCHO as seen from space indicates missing marine sources for hydrocarbons in current models, or is an artifact in the satellite retrievals caused by a spectral interference of light absorbing phytoplankton.

Here we present spectral proof for elevated CHOCHO concentrations over biologically active upwelling regions of the Pacific Ocean. We discuss the spatial and temporal variability, and compare our data with previously published satellite data and model predictions. We find CHOCHO is enhanced more than 3000km from the West Coast of South America, and conclude that such CHOCHO can not be explained by continental outflow of CHOCHO or precursor hydrocarbons emitted over land. Finally, we discuss a possible source mechanism for CHOCHO over the open ocean, and assess the implications of this novel chemistry indicated by CHOCHO over large parts of the open ocean, that is not currently represented in atmospheric models.

Secondary Organic Aerosol Formation from Green Leaf Volatiles

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Green leaf volatiles (GLVs) are an important group of chemicals released by vegetation which have emission fluxes that can be significantly increased when plants are damaged or stressed. A series of simulation chamber experiments has been conducted at the European Photoreactor in Valencia, Spain, to investigate secondary organic aerosol (SOA) formation from the atmospheric oxidation of the major GLVs *cis*-3-hexenylacetate and *cis*-3-hexen-1-ol. Liquid chromatography-ion trap mass spectrometry was used to identify chemical species present in the SOA. *Cis*-3-hexen-1-ol proved to be a more efficient SOA precursor due to the high reactivity of its first generation oxidation product, 3-hydroxypropanal, which can hydrate and undergo further reactions with other aldehydes resulting in SOA dominated by higher molecular weight oligomers. The lower SOA yields produced from *cis*-3-hexenylacetate are attributed to the acetate functionality, which inhibits oligomer formation in the particle phase. Based on observed SOA yields and best estimates of global emissions, these compounds may be calculated to be a substantial unidentified global source of SOA, contributing 1-5 TgC yr⁻¹, equivalent to around a third of that predicted from isoprene. Molecular characterization of the SOA, combined with organic mechanistic information, has provided evidence that the formation of organic aerosols from GLVs is closely related to the reactivity of their first generation atmospheric oxidation products, and indicates that this may be a simple parameter that could be used in assessing the aerosol formation potential for other unstudied organic compounds in the atmosphere.

Gas-phase Precursors to Anthropogenic SOA: Using the MCM to Probe Detailed Observations of Aromatic Photo-oxidation

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In the work presented, a detailed gas-phase photochemical chamber box model, incorporating the MCMv3.1 degradation scheme for the aromatic compound 1,3,5-trimethylbenzene (TMB), has been used to simulate data measured during a series of chamber experiments carried out in the Paul Scherrer Institute Aerosol Chamber in order to evaluate the mechanism under a variety of VOC/NO_x conditions.

The TMB mechanism was extracted from the Master Chemical Mechanism (MCM, <http://mcm.leeds.ac.uk/MCM>), a near-explicit chemical mechanism originally conceived to model ozone formation in Europe but now also employed as a benchmark mechanism in a wide variety of applications where chemical detail is required.

The chamber model was used in the interpretation of data recorded by the University of Leicester's Chemical Ionisation Reaction Time-of-Flight Mass Spectrometer (CIR-TOF-MS) a novel instrument used to provide comprehensive, high (mass and time) resolution measurements of TMB and its oxidation products. Supporting gas and aerosol measurements also enable us to explore the "missing link" between the gas and aerosol phases. Model-measurement comparisons have been used to gain an insight into the complex array of oxygenated products formed, including the peroxide bicyclic ring opening products (γ -dicarbonyls and furanones) and the O₂-bridged peroxide bicyclic ring retaining products (diol, ketone and nitrate). To our knowledge this is the first time these O₂-bridged species have been identified in the gas-phase. The model was also used to give insights into which gas-phase species were participating in SOA formation, with the primary and secondary peroxide products, formed primarily under NO_x-limiting conditions, identified as likely candidates.

Separating the Contributions of Black and Brown Carbon in urban Aerosols

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Until about a decade ago, black carbon (BC) was thought to be the only light absorbing substance in the atmospheric aerosol except for soil or desert dust. In more recent years, light absorbing polymeric carbonaceous material was found in atmospheric aerosols. This fraction was called brown carbon (e. g. Andreae and Gelencser, 2006). Because it absorbs very weakly in the longwave part of the visible spectrum, but more strongly at short wavelengths. As brown carbon is thermally rather refractory, it influences the split between organic carbon (OC) and elemental carbon (EC) in thermal methods, and, through its light absorption characteristics, leads to overestimations of BC concentrations.

In this study, the integrating sphere method (Hitzenberger et al., 1996) was extended to correct the BC signal for the contribution of brown carbon and to obtain an estimate of brown carbon concentrations. In the original integrating sphere (IS) method, the attenuation signal of an aerosol sample is converted to BC concentration using a calibration curve obtained with a commercial carbon black (Elftex 124). If the aerosol contains light-absorbing material other than BC, the IS method overestimates BC concentrations. In the new modification, the wavelength range of the IS was extended to enable also measurements at 402, 450, 550 and 650 nm. Using a second calibration curve obtained for a proxy of brown carbon (humic acid sodium salt) and an iterative method, the different wavelength dependences of the absorption signals are used to correct BC concentrations and to estimate brown carbon concentrations simultaneously.

The extended method was first tested on mixtures of test substances and then applied to atmospheric samples collected during biomass smoke episodes (Easter bonfires) in Austria. The resulting concentrations of black and brown carbon are compared to EC obtained with a widely used thermal method, the Cachier method (Cachier et al., 1989) and a thermal-optical method (Schmid et al., 2001), as well as to concentrations of humic like substances (HULIS) and to biomass smoke POM (particulate organic matter). Both the thermal methods were found to overestimate BC on days with large contributions of woodsmoke. During the days of the bonfires, brown carbon was found to contribute 35 - 54% to biomass smoke POM, while HULIS accounted for 32 to 52% of brown carbon. During these days, the Cachier method gave EC concentrations that were higher by a factor of 3.79 than the BC concentrations, while the concentrations obtained with the thermal-optical method were higher by a factor of 2.63.

A full description of this study was published by Wonschütz et al. (2009).

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In situ Spectroscopic Investigations on Organic Coatings after Heterogeneous Processing by Ozone in the Presence of simulated Sunlight

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Both aromatic carbonyl and phenolic compounds originating from biomass combustion and industrial processes are largely present in the atmosphere.

This work intends to quantify the variation in optical properties of aerosol by spectroscopic *in situ* measurements of the reaction of ozone with a mixture of typical biomass burning compounds occurring on a model surface of an aerosol in the presence of simulated sunlight.

UV-VIS spectra taken before and after treatment of the particles show development into the visible (yellow colour) after prolonged ozone and light exposure of the particles coated with the mix of 4-CB/4-CB. Changes in optical properties of the aerosol components are reported, and variations of spectroscopic features are discussed. We show that the reaction of 4-phenoxyphenol (4-PP) and 4-carboxybenzophenone (4-CB) does produce light absorbing species in the solar spectral range.

Chemical changes on the coated surfaces were identified by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, and we suggest formation of humic-like substances comparable to those reported in continental aerosol.

Cross-Activation of atmospheric Pollutants – Reactions coupled with Autoxidation of S^{IV}

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Sulphur dioxide is a pollutant and a trace component of the atmosphere that became a little forgotten, as its anthropogenic emissions had been significantly reduced in the developed countries. Actually, it never disappeared completely, and even attracted some attention again. Organosulphates discovered quite recently in atmospheric aerosol and rainwater samples can be related to sulphur dioxide or to products of its oxidation. Sulphur dioxide itself increased the yields of aerosol produced from heterogeneous transformation of isoprene [1]. Isoprene inhibited the aqueous-phase chain autoxidation of sulphite ions, apparently scavenging the sulphate radical-anions responsible for the chain propagation [2].

This poster summarizes the results of a research project that had been carried out in relation to INTRON programme. The main objective of this project was to show that transformation of sulphur dioxide could initiate the transformation of several other pollutants and induce the formation of new trace components of the atmosphere. The idea refers to phenomena observed in atmospheric chemistry for long time, but is far from being fully exploited. Thus, we followed the transformation of chlorophenols, nitrophenols and isoprene, which took place when these compounds were placed in aqueous solutions, in which autoxidation of sulphite ions (which form upon dissolution of sulphur dioxide) catalysed by manganese(II) sulphate or iron(III) sulphate was realised. We found, that chlorophenols and nitrophenols inhibited the S^{IV} autoxidation. Using the method of reversed rates, we determined the rate constants for reactions of these chlorophenols and nitrophenols with sulphate radical-anions [3,4]. The rate constant for the reaction of isoprene with sulphate radical-anions was determined before, so we focused on products the reaction yielded – the unsaturated sulphate and sulphite esters of isoprene derivatives [5]. The sulphate esters were likely precursors of organosulphates detected by other groups in chamber experiments and field samples, while the sulphite esters were observed for the first time. We also suggested the mechanism of transformation and verified it successfully against the experimental data, using computer simulation.

The results fill the gaps in kinetic and mechanistic knowledge of reactions that possibly contribute to atmospheric transformation, and indicate the possible sources of atmospheric organosulphur compounds. Realisation of the investigated reactions in real atmospheric systems has to be evaluated by further modelling studies.

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Bulk Reaction limited Uptake of NO₂ by Aerosols containing Hydroquinone and Gentisic Acid

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The uptake kinetics of nitrogen dioxide (NO₂), a major trace gas in the atmosphere, by deliquesced aerosol particles containing hydroquinone (1,4-dihydroxybenzene) or gentisic (2,5-dihydroxycarboxylic) acid has been quantified at 40% relative humidity and 23°C in a flow tube reactor. The experiments were performed using the short-lived radioactive tracer ¹³N. Results indicate that the uptake coefficient for NO₂ could be as large as $\sim 6 \times 10^{-3}$ for hydroquinone disodium salt aerosol, that exceed previously reported data in the range of $10^{-4} \div 10^{-3}$. The measured time dependence of NO₂ uptake was fitted using a kinetic model taking into account reactant consumption in the particle phase, and keeping the bulk accommodation coefficient, alpha, and the rate constants for the reaction of dissolved NO₂ with the deprotonated forms of the mentioned phenolic compounds as variables. We obtained $\alpha_b = (2.4 \pm 0.5) \times 10^{-2}$ from the best model fit. For hydroquinone, the rate constant agreed well with literature. For gentisic acid, the second-order rate constant was $k_2 = (3.2 \pm 0.2) \times 10^8 \text{ L mole}^{-1} \text{ s}^{-1}$. The data are consistent with bulk reaction limited uptake, without indication for a surface component in the kinetics.

Aging of a Model technogenic Aerosol formed from Combustion Ash: a Chamber Study

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For the evaluation of environmental and health effects of oil shale processing, information is needed on technogenic aerosols formed from fly ash (FA) emissions during combustion of this kind of fossil fuel. The former set of experiments on atmospheric behavior of FA as particulate matter was performed with ash from pulverized firing (PF) technology of combustion in Narva Power Plants LTD (Estonia). Recently a new innovative technology, circulating fluidized bed (CFB) combustion of oil shale, has been introduced.

The present experiments were conducted in a big (270 m³) dual outdoor Teflon film smog chambers of University of North Carolina (UNC) at Chapel Hill (USA) under normal meteorological conditions (temperature, humidity, sunlight), which were approximately similar to Estonia. The campaign started by injection of CFB combustion FA into the chamber. The size distribution (from 3.2 nm to 20 µm) and number concentration of particles were monitored during the experiment. It has to be pointed out that the CFB ash has different character and very fine structure compared with PF ash. The results clearly demonstrate that during approximately one hour after the injection of FA the fraction more than 5 µm of aerosolized particles settled out. For the fine fractions (less than 0.5 µm) of FA the coagulation phenomena has previously observed during our trial, indicating the formation of a more stable secondary aerosol.

Thus, the aerosol from the CFB combustion ash could be more stable and the long-range transport more pronounced compared with PF fly ash. The role of respirable fraction of particles, which contributes most of the health effects of the aerosol, is significantly higher in FA aerosols formed by using the CFB technology for the energy generation than that from PF process.

Future plans: Generation of a similar technogenic aerosol for investigation adverse health effects by targeted exposures of a lung cells system, directly interfaced with the smog chamber. Participation of Dr. K. G. Sexton (Prof. H.E. Jeffries group, UNC) in the collaborative study on this issue is crucial.

ET (grant 2558) and UK (grant 2559) thankfully acknowledge the support received from the *ESF Program INTROP*. GU has been granted by an Estonian mobility grant *Kristjan Jaak*.

CAPRAM Modelling of the Physico-Chemical Cloud Processing of tropospheric Aerosols

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Keywords: multiphase chemistry modelling, aerosol cloud interaction

Clouds and deliquescent particles are a complex multiphase and multi-component environment with simultaneously occurring gas and aqueous phase as well as heterogeneous chemical transformations which potentially alter the physico-chemical composition of tropospheric aerosols. Moreover, chemical cloud interactions contribute significantly to the physico-chemical aerosol processing together with significant effects on the whole multiphase oxidation budget. In order to improve the still limited understanding of the cloud chemistry processing, detailed model studies using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM; Wolke et al. [2005]) have been performed.

The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model. In the chemistry model, the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i [Karl et al., 2006; Herrmann et al., 2005] with about 1100 processes was applied incorporating a detailed description of the tropospheric multiphase processes. Simulations were carried out for different environmental conditions using a non-permanent meteorological scenario. Furthermore, simulations were performed with and without aqueous phase chemistry to study the effects of aerosol-cloud interactions. The model results have been analysed including time-resolved source and sinks studies particularly focused on multiphase phase radical as well as non-radical oxidants and multiphase oxidations of C₂–C₄ organic compounds.

The model studies show significant effects of multiphase cloud droplet and aqueous aerosol interactions on the tropospheric oxidation budget for polluted and remote environmental conditions as well as influenced VOC oxidations due to the changed oxidation budget within the clouds. Furthermore, the simulations implicate the potential role of deliquescent particles to act as a reactive chemical medium due to the in-situ aqueous phase oxidant productions. Moreover, the model studies show the importance of the aqueous phase for the formation of higher oxidised organic compounds such as substituted mono- and diacids. In particular, the aqueous phase oxidations of methylglyoxal and 1,4-butenedial were identified as important OH radical sinks under polluted environmental conditions contributing to the production of less volatile organic compounds and thus the organic aerosol particle mass. Further, the in-cloud oxidation of methylglyoxal and its oxidation products represents an efficient sink for NO₃ radicals in the aqueous phase. Additionally, the model studies have shown in-cloud organic mass productions up to about 1 µg m⁻³ preferably under polluted day time cloud conditions mainly due to OH initiated multiphase oxidation processes.

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In-Cloud Processing of Secondary Organic Aerosols

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Clouds continuously appear and disappear through evapo-condensation cycles. Particles and water soluble pollutants become dissolved in cloud droplets where they undergo photochemical reactions. When clouds dissipate, the pollutants evaporate and the low volatile compounds condense to new particles. This is a new route for secondary organic aerosols (SOA) formation which is potentially very important, but has never been experimentally investigated before.

We performed the following experiments sequentially in the PSI smog chamber and in an aqueous phase photoreactor (brought from LCP-Marseilles) to simulate multiphase processes: 1) gas-phase photooxidation of three different VOC (isoprene, 1,3,5-TMB, and α -pinene), leading to the formation of particles (SOA_{gas}); 2) particle-to-liquid transfer of soluble species using filters followed by water extraction ; 3) aqueous-phase photoreaction of the obtained water extracts, in the aqueous phase photoreactor ; and 4) cloud evaporation and formation of new SOA (SOA_{cloud}), simulated by nebulization of the solutions.

Physical and chemical properties of SOA_{gas} and SOA_{cloud} were measured to determine the impact of multiphase photooxidation of the studied VOC on the formation of SOA in the atmosphere. The first results show that, depending on the initial VOC, the chemical composition of SOA_{gas} can be very different from that of SOA_{cloud}.

CAPRAM Modelling of the Speciation and Redox-Cycling of Iron in deliquescent Particles and Cloud Droplets

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Keywords: multiphase chemistry modelling, aerosol cloud interaction

The most abundant TMI in tropospheric particles is iron which plays a crucial role in the aqueous phase chemistry of fog and cloud droplets. The redox-cycling of iron is responsible for many chemical interactions such as the HO_x/HO_y processing. However, still large uncertainties of TMI chemistry exist and less is known about the TMI speciation in the particulate phase. To this end, the iron speciation and redox-cycling in deliquescent particles and cloud droplets were investigated in more detail by means of model studies using the SPectral Aerosol Cloud Chemistry Interaction Model (SPACCIM; Wolke et al. [2005]). The parcel model SPACCIM includes a complex microphysical and multiphase chemistry model. In the chemistry model, the multiphase mechanism RACM-MIM2ext/CAPRAM 3.0i [Karl et al., 2006; Herrmann et al., 2005] with about 1100 processes was applied incorporating a detailed description of the tropospheric multiphase processes. Simulations were carried out for different environmental conditions using a non-permanent meteorological scenario. The model results have been analysed including time-resolved source and sinks studies. The model studies were particularly focused on temporal variations in the iron speciation and redox-cycling in the condensed phase including its importance for other important chemical subsystems such as the multiphase $\text{HO}_{x,y}$ and organic chemistry. For this purpose, sensitivity studies have been performed on the importance of the water soluble iron content for the aqueous phase oxidation capacity and chemical processing of organic compounds.

The model results have shown characteristic diurnal profiles of the iron speciation in both deliquescent particles and clouds. Moreover, up to about 20 to 50 % of the soluble iron is shown to be still present as Fe^{2+} during the night which reflects an efficient nighttime iron-redox-cycling under polluted environmental conditions. Performed comparisons with available cloud water measurements and former model calculations revealed reasonable agreements as well as some differences.

The model results have additionally pointed out considerable differences between the iron cycling in deliquescent particles and cloud droplets. The model results revealed chemical differences in the sink and source reactions caused by different pH conditions as well as the different HO_2/O_2^- budget in the two aqueous environments. Moreover, the model results implicated the role of deliquescent particles to be a reactive medium for the TMI redox-cycling which is potentially important for other chemical subsystems. Under urban conditions, the modelled total daytime fluxes in the deliquescent particles are partly two times larger than in daytime clouds.

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Graphical Interface Development for chemical Mechanism Modelling in Simulation Smog Chambers

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The degradation in the atmosphere of VOCs generates a great variety of secondary pollutants that have adverse effects on climate, air quality and human health. Since the atmosphere is a highly complex reactor, field measurements only give us information related to specific locations and time. For this reason, in order to interpret the individual chemical processes that take place and their interactions, we have two essential tools; *Simulation smog chambers*, to improve our knowledge on the chemical mechanisms and provide their parameters, and *Models*, to provide the necessary framework for integration of our understanding of individual processes and study their interactions under a variety of realistic conditions. In this sense, the European Photoreactor EUPHORE (CEAM, Valencia, Spain) is one of the major outdoor smog chambers in the world that uses natural light for the study of photochemical processes. The facility consists of two half-spherical photo-reactors, with a volume of $\sim 200 \text{ m}^3$ each. For the simultaneous detection of the reactants and products, the chambers are equipped with an array of analytical techniques, ranging from monitor type, GC-techniques and particle measurement equipment to sophisticated *in-situ* optical measurement devices.

In this contribution, a graphical interface created for the modeling of the chemical mechanisms studied in simulation smog chamber is presented. The work was supervised by Professor M. J. Pilling and is one of the main results obtained during two visits (September 2006 and November 2008) to the University of Leeds supported by the INTROP programme to M. Vazquez.

The interface is based on the Open Source MCM Box Model developed in FORTRAN at the University of Leeds. It avoids the direct modification of the model code by the user and enables an easy configuration of its parameters. It covers the setting of the experimental conditions (species, chemical mechanism, initial concentrations, photolysis frequencies, environmental conditions, etc), model parameters (start time, number of steps and step size, data interpolation method, etc) and sensibility analysis tests as a Rate Of Production Analysis (ROPA) of the species of interest established by the user. To develop the graphical interface two main programs were used; Anjuta 1.2.4a (<http://www.anjuta.org>) and Glade 2.12.1 (<http://glade.gnome.org>).

Time-resolved Measurement of Aerosol Elemental Concentrations in the Indoor Working Environment

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We have measured elemental concentrations of aerosols with two-hour time resolution in two different types of working environment: a chemistry lab dealing with ceramics and nanomaterials and in a medium sized machine workshop. A non-stop 10 days and 12 days sampling was performed at each place respectively, to trace the concentration trends throughout the non-working/working and weekday/weekend periods. Supplementary measurements of PM10 aerosols with 2 days sample collection time were performed with standard Gent PM10 sampler to compare elemental concentrations from time integrated samples with the time-integrated concentrations obtained by the time-step sampler. The concentrations were determined a posteriori by analyzing x-ray spectra of aerosol samples emitted upon 3 MeV proton bombardement. The PM10 samples taken in chemical lab were additionally inspected by scanning electron microscope (SEM) to determine chemical composition of single particles containing characteristic elements and in the workshop a simultaneous PM10 total mass sampling was performed. The elemental concentration sampling with hourly resolution is an excellent tool to study indoor air pollution: while sampling of the total PM10 mass concentration with a minute resolution may lack the potential to identify emission sources in a "noisy" environment, the time averaging on a day time scale is too coarse to cope with the working dynamics even if elemental sensitivity is an option.

Observations of Water Uptake in Ammonium Sulphate Particles using X-Ray Microspectroscopy

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Aerosols directly affect the radiation balance of the earth by absorbing and scattering radiation. The optical properties are influenced by the hygroscopic properties and the morphology of the aerosol particles, which strongly depend on their chemical composition.

While the overall chemical composition of the aerosol particles is known to some degree, the complex interplay between individual components as a function of humidity including the formation of separate phases, especially in internally mixed organic / inorganic particles, is poorly understood. Therefore, accurate identification of the behaviour of the single components or phases within individual particles during the uptake and release of water is necessary.

In this project we use X-ray microspectroscopy, which combines the microscopic and spectroscopic methods, to observe water uptake and release in individual micrometer-sized aerosol particles such as ammonium sulphate, partially mixed with organic compounds. We use a newly developed cell, where we deposit the aerosol particles (figure 1). This setup allows in situ studies of micrometer sized aerosol particles under controlled gas phase composition and temperature.

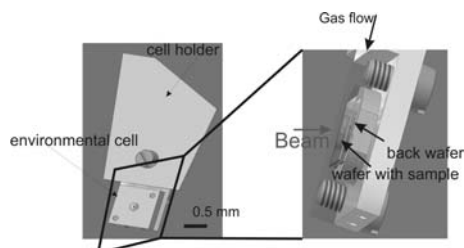


Figure 1. To the left: the environmental cell mounted on the cell holder. To the right: the lower part of the environmental cell where the aerosols might be collected.

The measurements are performed at a soft X-ray beamline with a microfocus (PolLux) of the Swiss Light Source (SLS) located at the PSI. Due to the excellent resolution of the microscope (35 nm) we have the possibility to map different functional groups of the individual compounds with a very high spatial resolution.

Here, we report results obtained with the environmental cell and ammonium sulphate particles as a well established test system. During water uptake and release, we can observe spectroscopic features, which can be used to understand in a qualitative way the structural bonding of water in these particles.

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Photo-Chemical Reactions in an urban Agglomerate Street Canyon studied by DIAL

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The real street canyon is a part of the north-south trunk road that passes through the centre of Prague and remains an unresolved environmental issue for the capital of the Czech Republic. The method of remote sensing was used to monitor phenomena related to atmospheric pollutants in this street canyon. The analysis of processes was carried out on the base of results of monitoring of NO₂ and O₃ concentration levels in the vertical profile above the street. A set of spatial measurements of pollutants distribution *during a day*, was realized by the combined DIAL/SODAR method and using spot analyzers appropriately located near the street canyon bottom. The measurements were performed under different meteorological conditions (autumn versus summer period). The analysis clearly proved that a purely physical approach does not provide a true description of reality because chemical reactions especially photo-chemical processes taking place in the street canyon atmosphere.

Influence of a Photosensitizer on the Aging of Succinic Acid Aerosol

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Keywords: photosensitizer, succinic acid, AMS

Ultraviolet or visible light absorbing organic constituents of atmospheric aerosols may act as photosensitizers for a number of chemical processes. Photosensitizers may be primary organics from combustion sources or be formed in situ during oxidation in the atmosphere. The significance of photosensitized processes has been established by showing enhanced uptake of atmospheric oxidants to organic films or aerosol particles.

A solution containing ammonium sulfate, succinic acid and benzophenone was nebulized. The aerosol flow passed through a photoreactor with approximately 9 min. residence time. The flow tube was coupled to a High Resolution Time of Flight Aerosol Mass Spectrometer (AMS) and two Scanning Mobility Particle Sizers (SMPS).

During the photooxidation experiments we observed changes to the ratio of m/z 44 to total organic mass and a loss of organic aerosol mass, while the flow tube was irradiated. This change in the 44 to total organic mass ratio is typically associated with the loss of carboxylic acid groups. This indicates chemical reaction occurring during the UV exposure. These effects seem to appear only in presence of the photosensitizer and scale with the light intensity. A detailed analysis of the available data will allow extracting more information on potential products of the light induced reaction. The results will be shown and discussed.

Angstrom Exponent in the UV range determined by Aerosol microphysical Properties

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Atmospheric aerosol plays significant role attenuation in UV radiation. However measurement of aerosol optical properties in UV are difficult and rather rare especially in deep UV (below 320 nm). In absence of measurements aerosol optical properties in UV are extrapolated from visible range by means of Angstrom Exponent. However values of angstrom exponent in UV are weakly recognized, some authors question negative values of the parameter. In this work influence of aerosol microphysical properties on angstrom exponent is shown. Influence of monomodal and bimodal aerosol size distribution is discussed for different values of refractive index. Classes of the aerosol with negative angstrom exponents are also found.

Determination of Particulate Matter Deposition Sources

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Fine and ultra fine particles represent hazard to human health due to their deep penetration in the respiratory system. That is why a lot of research interest is focused on fine particles. But also dust emissions of larger particles (10 - 20 μm or more) from various anthropogenic sources such as ore depots, coal pits or even quarries should also represent matter of concern due to their nuisance for residents living in near by areas. Inhabitants of Ankaran city (at Slovenian coast) and its surroundings have complained about the pollution of their residential area with emissions from the terminal EET (mainly coal and iron ore particles) in the Port of Koper for several years. Particulate matter depositions are visibly perceived on their yards, places of residence, vegetables and fruit trees. For that reason the impact of dust pollution from coal and iron ore handling on surroundings area will be presented. At the European Energy Terminal (EET) in the Port of Koper, large amounts of coal and iron ore are handled and warehoused. The storage capacity of the landfill is 450,000 tons for coal and 350,000 tons for iron ore. The area covered by the coal and iron ore is 108,500 m^2 . In the study 10 sampling sites in the area of Ankaran, Koper and its surroundings were included. The collection of particulate matter deposition was conducted with the standard Bergerhoff precipitators according to VDI 2119 part 2 (1996) - Measurement of particulate precipitations determination of dust precipitation with collecting pots made of glass.

Samples were collected and analyzed (gravimetrically) on the 1st and 15th day of each month for a one year period from December 2007 to December 2008. Gravimetric analyses was performed according to VDI 2119 part 2 (1996) guidelines. During the sampling period the total amount of particulate matter deposition at all sampling sites in the area of the municipality of Ankaran, Koper and surroundings never exceeded the recommended emission value of 350 mg/m^2 day. The shape and size of the particles collected over a 12-month period and some of the elements they contained were determined by electron microscopy coupled with energy-dispersive x-ray fluorescence spectrometry. According to the previous studies (Poljšak *et al.*, 2006; ARSO, 2005) the quantity of particulate matter depositions depends mostly on weather conditions, especially the strength and direction of the wind and also the quantity of rainfall, which determined the dryness of the terrain and also dryness of coal and iron ore stockpiles. For that reason a possible correlation between particulate matter deposition, weather conditions and cargo manipulation will be analysed. Additionally the $^{13}\text{C}/^{12}\text{C}$ ratio in samples will also be analysed to determine the sources of particulate organic matter. As far as we know two new approaches have been implemented for the first time ($^{13}\text{C}/^{12}\text{C}$ ratio and electron microscopy coupled with energy - dispersive x-ray fluorescence spectrometry) for determination of the origin of coal in dust samples.

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Radical, Humidity and Temperature effects on SOA Formation from Ozonolysis of Monoterpenes

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Secondary organic aerosol (SOA) formation accounts for a significant fraction of ambient tropospheric aerosol (Hallquist *et al.*, 2009). In this work special emphasis is on SOA produced from oxidation of biogenic compounds. In the atmosphere these compounds are oxidised primarily by ozone, OH radicals and NO₃ radicals. In the degradation process compounds with low volatility can be formed which may undergo gas-to-particle conversion, hence contributing to the formation of SOA. One important group of compounds contributing to SOA formation is the monoterpenes (C₁₀H₁₆), where globally α -pinene and limonene are the most abundant. In this work the impact of temperature, relative humidity (RH) and radical chemistry on the aerosol formation from ozonolysis of limonene, Δ^3 -carene, α -pinene and β -pinene have been investigated. The experiments were conducted by using the G-FROST (Göteborg-Flow Reactor for Oxidation Studies at low Temperatures) set-up. This set-up consists mainly of a laminar flow reactor (length: 1.9 m and i.d:10 cm) and a scanning mobility particle sizer (SMPS) system where particle number and mass size distributions were obtained. This is a set-up where temperature, relative humidity and concentrations can be carefully controlled (e.g. Jonsson *et al.*, 2008). Figure 1 illustrates the effect of water and scavenger on SOA formation.

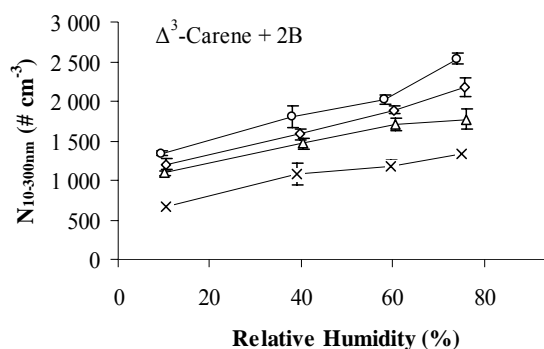


Figure 1. Effect of OH scavenger concentration on the number of particles formed in the ozonolysis of Δ^3 -carene. The concentration is increasing in the order circles, diamonds, triangles and crosses.

The results presented are for different reaction temperatures (243 - 298 K) and for a range of relative humidities (0 - 80%). In addition, the use of OH-scavengers, 2-butanol or cyclohexane and without any scavenger in the system, will demonstrate another important topic showing the evidence of OH radical production from the ozonolysis at low temperatures. The results are discussed in relation to the current knowledge of the degradation mechanism and structural differences between the monoterpenes investigated.

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Light induced Multiphase chemistry of Gas Phase Ozone on Aqueous Pyruvic and Oxalic Acids

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Both pyruvic and oxalic acids are common constituents of the atmospheric aqueous phase and they are simultaneously exposed to the sunlight and atmospheric oxidants.

In this work time series samples from photochemical batch multiphase reactions of the mixture of pyruvic acid/oxalic acid (PA/OA) and gas-phase ozone under simulated sunlight were analyzed by high liquid chromatography equipped with UV detector (HPLC-UV) and electrospray ionization mass spectrometry (ESI-MS) for product formation. The HPLC-UV analytical technique revealed a broad band following the prolonged simultaneous ozone and light exposure of the aqueous mixture consisted of pyruvic and oxalic acid. Reaction products consistent with an oligomer system were identified by ESI-MS when the aqueous mixture of pyruvic acid and oxalic acid was simultaneously exposed to gas-phase ozone and irradiated by simulated sunlight in the time period of 6-12 hours.

We propose that in our reaction system consisted of PA/OA a key to control the photo induced oligomerization process is the the photoinitiator (in this case pyruvic acid), which absorbs light (in the tropospheric actinic window, $\lambda > 300\text{nm}$) and thus, generates active radicals to further initiate the oligomerization.

Moreover, the reaction system proposed in this study may contribute to the formation of small volatile organics that are emitted in the gas phase and further participate in the secondary organic aerosol formation.

Secondary Organic Aerosol Formation from Anthropogenic and Biogenic Sources: Bridging Field and Smog Chamber Experiments using Nuclear Magnetic Resonance (NMR) Spectroscopy

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Proton-nuclear magnetic resonance (¹H-NMR) spectroscopy provides characterization of the organic fraction of the aerosol in terms of integral chemical properties of complex organic mixtures, thus allowing to overcome the recovery limits of the analytical techniques based on molecular characterization. Moreover, analogously to aerosol mass spectrometry (AMS), ¹H-NMR spectroscopy can be used to fingerprint different "types" of organic aerosols and associate them to specific sources. We have derived the ¹H-NMR characteristics of SOA produced during photooxidation and ozonolysis experiments from biogenic and anthropogenic VOCs in the PSI and SAPHIR reaction chambers. We have then used the above spectra to interpret the ¹H-NMR data obtained during field experiments, both in a pristine forested environment (Hyytiälä) and in polluted rural areas (Po Valley). Preliminary results indicate that spectroscopic techniques such as NMR spectroscopy can profitably complement AMS in organic aerosol source apportionment studies.

Photolysis Studies of 2-Nitrophenol Using Natural Sunlight

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The possible contribution of nitroaromatic compounds to forest decline created the impetus for the study of their atmospheric behavior. These compounds are directly emitted to the atmosphere and are also formed in situ in the atmosphere by secondary chemical processes.

The photolysis of 2-nitrophenol with natural sunlight has been studied in the European smog photoreactor (EUPHORE) under different conditions. The effects of the presence and the absence of NO_x and also an OH radical scavenger on the aerosol and ozone formation from the photolysis have been investigated.

One of the main results is the high aerosol yield (30 – 56 %) obtained from the photolysis reaction, demonstrating that 2-nitrophenol photolysis is a potentially important contributor to the SOA formation observed from the photooxidation of aromatic hydrocarbons. The size distribution of the particles has shown that the behavior of the nucleation and growth processes of the aerosols depended on the atmospheric oxidant conditions selected. Moreover, the aerosol density was calculated from two on-line measurement systems: SMPS (scanning mobility particles sizer) and TEOM (tapered element oscillating microbalance). The measured density which ranged between 0.8 – 1.2 g/cm³ was found to be dependent on the oxidant conditions.

Increasing our understanding of the chemical behavior and properties of these compounds, their physico-chemical processes and their products is vital for properly assessing their role in pollution and climate change.

Cloud Droplet Activation and Volatility of SOA Particles produced by the Photooxidation of Isoprene

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The cloud condensation nuclei (CCN) properties of mixed particles composed of sulfate and condensed-phase products from OH radical-initiated photooxidation of isoprene were investigated in the continuous-flow Harvard Environmental Chamber. CCN activity was measured for a range of VOC and NO_x concentrations for particles having diameters of 70 to 150 nm. Steady-state isoprene concentrations in the chamber prior to reaction were varied between 50 and 200 ppbv. NO_x concentrations in the chamber were varied between <1 and 38 ppbv. A two-component (organic/sulfate) Köhler model was used to calculate CCN activation curves. The observed activation curves were well predicted using a single set of physicochemical parameters for the organic component. CCN activity was also measured for particles produced in the chamber and subsequently passed through a thermodenuder with temperatures of 60° and 100°C. The observed decrease in CCN activity suggests that a fraction of the organic component is insoluble and that the water-soluble species of the organic component have greater volatility. The results also suggest that the soluble organic fraction increases as NO_x concentrations increase, which may be explained by an increased presence of nitrates in the condensed phase. Critical supersaturations calculated using the two-component Köhler model with parameters inferred from this study for particles not thermally treated agree with those measured over central Amazonia during the wet season, thus implying that realistic treatment of cloud formation over pristine regions may be achieved using a simple Köhler model.

CCN Activity and Droplet Growth Kinetic Measurements in Spring and Summer Arctic Air Masses

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We present an overview of cloud condensation nuclei (CCN) measurements of fresh Canadian forest fire plumes sampled during the Summer phase of the 2008 NASA Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS) campaign, as well as measurements of Springtime aged and pristine arctic air masses and aged biomass burning plumes transported from the mid-latitudes conducted during the 2008 NOAA Aerosol, Radiation, and Cloud Processes affecting Arctic Climate (ARCPAC) campaign. Continuous-Flow Streamwise Thermal Gradient CCN counters were deployed aboard the NASA DC-8, NASA WP-3B, and NOAA WP-3D aircraft and data were obtained at multiple climatically-relevant supersaturations (0.1-0.6%). CCN number concentration and droplet growth kinetics were characterized using theory to determine the influence of organic species on them. The data indicate that organics compounds have a strong influence, particularly for fresh biomass burning plumes and pollution layers transported from the mid-latitudes. In addition, the data suggest that CCN properties differ for plumes from flaming and smoldering fires, with properties that can be easily parameterized. The comprehensive nature of the CCN measurements (taken from multiple platforms and across a wide geographic and temporal area) make this a valuable data set for constraining current uncertainties associated with predicting CCN and cloud droplet number concentrations for pollution-influenced Springtime and Summertime arctic air.

Scanning Flow CCN Analysis for Fast Measurements of CCN Spectra

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The Continuous-Flow Streamwise Thermal-Gradient Cloud Condensation Nuclei Counter (CFSTGC) is rapidly becoming the instrument of choice for both laboratory and field measurements of cloud condensation nuclei (CCN). Typically, the instrument is operated at a constant flow rate, and supersaturation is adjusted by changing the column temperature difference, which is relatively slow (20-40 seconds for the column temperatures to stabilize and as much as 3 minutes for the OPC temperature to stabilize) and may introduce particle volatilization biases (Asa-Awuku et al., 2009). Data collected during transient periods are often discarded, which is particularly problematic for aircraft measurements in heterogeneous environments. We present a new mode of operation, termed “Scanning Flow CCN Analysis” (SFCA), in which the flow rate is changed over time in the flow chamber, while maintaining a constant temperature gradient; this causes supersaturation to continuously change, allowing the measurement of a CCN supersaturation spectrum much more quickly over timescales relevant for airborne measurements (~10-60 seconds and potentially even less) and without loss of data continuity. SFCA is demonstrated using numerical simulations and measurements of both calibration and ambient aerosol.

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A Physically-Based Parameterization of Ice Cloud Formation for Large-Scale Simulations

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This study presents a comprehensive ice cloud formation parameterization that computes the ice crystal number, size distribution, and maximum supersaturation from precursor aerosol and ice nuclei with any size distribution and chemical composition. The parameterization provides an analytical solution of the cloud parcel model equations and accounts for the competition effects between homogeneous and heterogeneous freezing, and, between heterogeneous freezing in different modes. The diversity of heterogeneous nuclei is described through a nucleation spectrum function, which is allowed to follow any form, and depends on the surface area, chemical composition, and size distribution of the precursor, insoluble aerosol. The parameterization reproduces the predictions of a detailed numerical parcel model to within $-2.0 \pm 8.5\%$ for conditions of pure heterogeneous freezing, and, $4.7 \pm 21\%$ when both homogeneous and heterogeneous freezing were active. Apart from its rigor, excellent performance and versatility, the formulation is extremely fast and free from requirements of numerical integration.

Real-time Measurements of single Particle Composition at Cork Harbour, Ireland

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Although several studies have been performed on the chemical composition of individual particles in various remote and urban environments, in-port sites have received comparatively little attention. Emissions from shipping traffic in particular remain relatively unconstrained and thus may significantly affect local and regional air quality in port cities. A TSI 3800 Aerosol Time-of-flight Mass Spectrometer (ATOFMS) was co-located with a range of real-time instrumentation for the measurement of gas and particle phase species at an in-port site in Cork Harbour for three weeks in August 2008. The ATOFMS was fitted with an aerodynamic lens for the measurement of particles in the aerodynamic diameter range 100-3000 nm. Over 500,000 particle mass spectra were generated during the campaign and divided into various classes based on their composition. One class attributed to shipping traffic accounted for approximately 2.5% of the particles successfully measured by the instrument. The particles were found to contain elemental carbon, organic carbon, calcium, vanadium and primary sulfate. The temporal profile for this class exhibited sharp peaks and only increased when the wind was from a southwesterly direction, passing over a nearby shipping lane. Simultaneous real-time scanning mobility particle sizer (SMPS) measurements demonstrated that the vast majority of these freshly emitted particles were in the ultrafine mode and thus were not observed by the ATOFMS. Therefore the number fraction of particles sampled and attributed to shipping traffic in the local area is considered to be very much a lower limit.

On the Origin of high Aerosol Optical Thickness Episodes at Belsk, Poland, 1992-2008 based on the Brewer Spectrophotometer Data.

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Analysis of seasonal variation of aerosol optical thickness (AOT) in the UV range (320 nm) measured at Belsk, Poland during 1992-2008 reveals two distinct maxima: in April and in August. Practically all of the days with the highest recorded AOT (up to 2.0) occur in these or adjacent months. Measurements of AOT have been performed by the Brewer Spectrophotometer No 064. The measurement results are in good agreement with those obtained from the collocated Cimel sunphotometer operating within the AERONET network. Analysis of backward trajectories of air coming over Belsk in conjunction with analysis of fire maps from Fire Information For Resource Management System show that these seasonal maxima are connected with advection of polluted air from seasonal biomass burning regions in Eastern and Southern Europe.

Mie Lidar for Aerosols and Clouds Monitoring at Otlica Observatory

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Aerosol and cloud density are the most important atmospheric parameters, which significantly influence the atmospheric conditions. It is most meaningful to study the spatial and temporal properties of the aerosols and clouds.

In recent years, lidar techniques for remote sensing of the atmospheric parameters have been greatly improved. Like the lidar system of the Pierre Auger Observatory in Argentina, the Mie lidar built at Otlica Observatory (45:93 N, 13:91 E, 945m a.s.l.) in Slovenia employs the same hardware, including the transmitter, the receiver, and the DAQ system. Due to its high-power laser, large-diameter telescope, and the photon-counting data-acquisition technique, the Mie lidar has the potential ability to measure the tropospheric and stratospheric atmospheric conditions, and it is suitable for monitoring of the changes in the cirrus clouds and atmospheric boundary layer.

Recently the routine experiments have been done. Through the techniques of event averaging, noise elimination, and data-gluing, the far end of probing range is extended up to 40 km. Time-height-intensity plot of the lidar backscatter signal shows the change of the atmospheric conditions, especially the motion of the cirrus clouds.

The global distribution of GEM and GOM concentrations in the marine boundary layer

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All known forms of mercury are toxic to humans but especially organic mercury compounds are highly toxic (WHO 2000).

The anthropogenic emission of mercury to the environment has been extremely variable during the last 100 years due to (Hylander and Meili, 2003; Pacyna and Pacyna 2002, AMAP UNEP report, 2008). West Europe and North America were previously the main emitters of mercury but now the emission is moving towards east e.g. to China due to increased coal combustion (Pacyna and Pacyna 2002).

Once mercury is emitted to the atmosphere it is believed to have a long lifetime, so that it can be transported worldwide and is e.g. found in the Arctic (Skov et al. 2004, 2006). However, the mechanism by which it is removed from the atmosphere is not clear (Ariya et al. 2008). Therefore it is very important to determine the distribution of the various form of mercury in the global atmosphere.

A TEKRAN 2537A mercury vapour analyzer with a TEKRAN 1130 mercury speciation unit were used to measure gaseous elemental mercury (GEM) and gaseous oxidized mercury (GOM) during an eight and a half month circumnavigation expedition. The cruise data give a global overview of GEM and GOM distribution in the marine boundary layer (MBL). These data were supplemented with simultaneous measurements of meteorological data, O₃, CO, and NO/NO_x. On-going is analysis of the measurements and comparison with results from the GEOS-Chem mercury model.

The global extent of the data makes it possible to test hypotheses within the model, regarding the dynamics of mercury in the MBL, to an extent that have not been done before. Like earlier cruises, we observe significantly higher background concentrations of GEM in the northern hemisphere than the southern hemisphere, a feature that is not described well in the model. The GEM concentrations observed in the North Atlantic MBL are higher than can currently be explained by outflow from industrial regions and we explore how ocean circulation and geochemistry might explain this feature. The ability of GEOS-Chem to reproduce observed Hg/CO ratios is examined and the Hg/CO ratios and source regions observed during the cruise are used to evaluate current emission inventories. Further data analysis and test of model hypotheses on the basis of the cruise are ongoing.

High-Resolution Mass Spectrometry – a new Tool to advance Organic Aerosols Characterization

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It has been shown in the last years that high molecular weight compounds make up a significant fraction (10-50%) of the organic compounds in ambient aerosols [1,2]. The chemical nature and formation processes of these compounds are only poorly understood. To better understand the formation processes of organic aerosols in the atmosphere and estimate their influence on climate and health related issues a more complete knowledge of the organic components in the ambient aerosol is necessary.

High-resolution mass spectrometry allows determining unambiguously the elemental composition of compounds. Secondary organic aerosol (SOA) samples were generated in an indoor smog chamber at the Paul Scherrer Institut, Switzerland. The particles were sampled on Teflon membranes filters and measured after extraction with electrospray mass spectrometry. The mass accuracy of the mass spectrometer was typically better than 2 ppm. Spectra were acquired at a resolution of 400'000 at m/z 400 [3].

Several hundred peaks in a mass range between m/z 200-700 were detected. Often within a few millidalton 2-3 peaks with totally different elemental composition are measured emphasizing the necessity for high-resolution measurements to elucidate the components in complex samples such as SOA. The mass spectrum is clearly divided in a range with low-molecular weight compounds ($m/z < 300$) and a high molecular weight (or oligomer) range ($m/z > 300$). The elemental composition of the majority of all peaks could be assigned. Most compounds in alpha-pinene-ozonolysis-SOA have high O:C ratios in the range of 0.4 - 0.6. Monomers have on average a higher O:C ratio than dimers and trimers, suggesting a condensation reaction leading from monomers to small co-oligomers. A program developed in-house was used to identify potential monomers in the spectrum. Up to 80 different monomers were identified with this procedure, which agreed well with the peaks found in the monomer region of the spectrum.

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The EUROCHAMP Database of European Atmospheric Simulation Chambers

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The Environmental Chamber Studies Database is an initiative within the EUROCHAMP project (Integration of European Simulation Chambers for Investigating Atmospheric Processes) to provide a practical tool for facilitating the interchange and comparability of the kinetic and mechanistic information obtained in the different European chamber experiments. This project is an integrated infrastructure initiative within the Sixth Framework Programme. The network group currently consists of 13 individual partner institutes operating in total more than 25 simulation chambers used for investigations related to atmospheric transformation processes.

This database is based on a decentralized concept. That means that a central search engine holds the key information in the data records, thus enabling an intelligent search within this information. After a successful search the database provides access to a static standard html page which provides the links to the individual files on the server generated in a particular experiment. These original data sets are located and maintained at each of the participating institutes. The central search engine is hosted at the CEAM Foundation and it is accessible through the main website of the EUROCHAMP project: <http://www.eurochamp.org>, at the link: Data Base or directly through: <http://eurochamp-database.es/>

In order to minimise the investment costs required to finance database software packages and hardware facilities for the creation and installation of the database servers, open source software packages have been used. The use of open software ensures its durability and robustness. In addition, the data introduced by the EUROCHAMP partners use a common ASCII format-Eurochamp Data Format (edf)- which is intended to be readable by all the users and easily processed by computer programs. A description, help files, and interactive tools for creating, testing and processing edf-files have also been developed.

At the moment the database contains more than four hundred and fifty records, and the number of records is expected to increase by at least one hundred per year. More than fifty users from twelve different countries, including China, are registered currently. The use of the database, and therefore to the data contained in it, is open to the whole scientific community, free of charge although registration is a requirement prior to its use. Nowadays, only institutions that belong to the EUROCHAMP consortium can introduce data, although other external institutions will be able to introduce data soon, if they wish, within the EUROCHAMP 2 project.

Improvements in Spectroscopy data processing at Faster production and better reliability of data analysis.

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EUPHORE (Valencia, Spain) is one of the major outdoor smog chambers existing for the study of photochemical processes that take place in the atmosphere, contributing to the development and optimization of chemical mechanisms. Within this context, FTIR has proven to be a very effective tool for the simultaneous determination of a great variety of compounds. Therefore, it is necessary to obtain reliable data as a basis for a better understanding of the studied processes involved.

Development of software for the analysis of spectroscopic data of complex gas mixtures has been done during the last years at EUPHORE. Within this context, an stay was done through the INTROP project at LISA, where the proposed algorithm was compared against other analysis methods. Specific probes were done to test the applicability of the algorithm for the retrieval of concentration profiles in the gas phase, in the presence of unknown interfering wide absorption compounds.

A case study is presented here on the analysis of samples containing HONO and also two nitrites that absorb in the same spectral range, where only one of their references is known. A comparison with other analysis methods is shown. The results of the tests show that the proposed methodology is a tool that both, decreases the number of freedom degrees to choose during the analysis and therefore the analyst intervention, and improves the quality of the retrievals – decreasing the error due to the interference - especially in complex gas mixtures with interfering compounds, a very common fact in IR samples.

Since experimental data are a feedback for models, the analysis algorithm showed will contribute to their improvement as well as to a better elucidation of the chemical mechanisms involved. Results are discussed.

Refractive Index Retrieval by a White Light Optical Particle Counter"

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A new approach to experimentally retrieve refractive indices (RI) of aerosol particles by a white light aerosol spectrometer (WELAS) optical particle counter (OPC) is presented. We propose a tandem differential mobility analyzer (DMA) – OPC system for RI derivation and instrument calibration, for both laboratory and field applications. This method was tested in the laboratory using substances with a wide range of optical properties. The obtained RIs correct the size data of the WELAS, and therefore, can be used for instrument calibration. The retrieved refractive indices are all in good agreement with expected values. Therefore, this is a robust method for calibration and RI retrieval of particles of sizes between 400-800nm.

Combining cw-CRDS and LIF with Laser Photolysis: Kinetic and Spectroscopy of HO₂ radical reactions

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OH and HO₂ radicals are key intermediates in the oxidation reactions of many radicals. A simultaneous and time-resolved detection of both radicals will largely simplify the understanding of these processes. We have therefore set-up an experimental technique able to do so: laser photolysis for radical generation coupled to LIF for OH radicals and cw-CRDS in the near infrared for HO₂ radicals. First results regarding the oxidation of aromatic hydrocarbons will be presented here.

Aromatic hydrocarbons are one of the largest families of VOCs in the atmosphere. As anthropogenic species, they are found principally in the urban atmosphere. Their emission originates particularly from vehicular traffic and solvent use. This class of hydrocarbons is supposed to be responsible for an important fraction of the photo-oxidant formation in industrialised countries. The other view-point of the effect of aromatic hydrocarbons on the environment is their impact on human health (e.g. benzene is carcinogenic). Moreover the photo-oxidation products of aromatic hydrocarbons are known to show toxic and mutagenic effects.

The proposed mechanism for the degradation of benzene in the atmosphere is known to be exclusively initiated by the attack of OH radicals, but there are still disagreements in the subsequent reaction mechanism. The OH-radical initiated oxidation of benzene was often investigated using H₂O₂ photolysis at 248 nm to generate OH radicals. But even though it is known that benzene absorbs at this wavelength, the direct photolysis of benzene was never studied or taken into account for the interpretation of the results.

We have studied the 248 nm photolysis of benzene in the presence of O₂ by laser photolysis / cw-CRDS and have found that HO₂ radicals are formed from a reaction of O₂ with excited benzene. An integration of this result in the interpretation of former laboratory studies might improve the knowledge of the oxidation mechanism of aromatic hydrocarbons.

EUPHORE: Formal Intercomparisons of Observations of Nitrous Acid (FIONA) Technical Workshop.

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Recent studies have indicated the important role that HONO plays in the atmospheric chemistry due to its implications in the photolysis processes, being an important source of OH radicals. Despite the huge number of techniques for measuring HONO, big discrepancies between data obtained with some of them have been previously reported. With the aim of elucidating these differences, in 3rd-5th March 2008, a HONO invited expert workshop was held in Wuppertal where the importance of the role of HONO in the atmosphere together with a review of the techniques used for its measurement were treated. As a consequence, it was agreed to carry out a formal intercomparison campaign for the detection of HONO: FIONA (Formal Intercomparisons of Observations of Nitrous Acid).

The campaign, that will be held at the EUPHORE chambers in May 2010, will involve the participation of more than 20 groups from different institutions and countries in Europe and USA. A wide number of techniques -ca. 16, covering spectroscopic, wet chemical and denuders- including recent developments, will participate in the campaign. Therefore, it became necessary to organize a technical workshop in order to better coordinate it and deal with the needed adaptations and modifications of the EUPHORE chamber.

The workshop took place at EUPHORE in November 17th-18th 2008 and was jointly supported by ESF (INTROP program) and EUROCHAMP project. It was attended by 23 participants from 12 different institutions of 6 countries. The topics treated included scientific, technical and logistical issues. The programme was organized into 3 main topics/sessions:

1. Justification of the need of carrying out the campaign and overview of techniques for measuring ambient concentration of HONO (established techniques and under development).
2. Adaptation of EUPHORE facilities for holding an intercomparison campaign of nearly all the available techniques for HONO detection. Technical issues.
3. Definition of the intercomparison campaign: Objectives, duration, experiments, etc

All the information on the workshop is available at the EUROCHAMP webpage:
http://www.eurochamp.org/events/2008/fiona_techn_ws

Comparative Measurements of Supersaturated Inorganic Aerosol using Optical Tweezers and an Electrodynamic Balance

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The size, phase and composition of an aerosol are known to be influenced by the relative humidity (RH) of the aerosol's surrounding environment. The changes to the physical or chemical properties of an aerosol may therefore alter the kinetics and/or mechanism of heterogeneous/multiphase reactions or the partitioning of gas-phase species to the aerosol. To gain further insight into the behaviour of aerosols at different RHs, particularly in the supersaturated regime, comparative growth measurements using two single particle techniques were performed. Although supersaturated droplets are ubiquitous in the atmosphere, there is a lack of work focussing on this RH regime. Therefore, one goal of this study was to perform comparative measurements of supersaturated sodium chloride aerosol using optical tweezers and an electrodynamic balance. Optical tweezers have primarily been used at RHs greater than 90%, therefore these measurements would also benchmark the performance of optical tweezers at atmospherically relevant RHs. Preliminary results comparing the growth of sodium chloride droplets in the supersaturated regime show good agreement between the two techniques. Further, the results demonstrate that optical tweezers can be used to perform experiments at more atmospherically relevant RHs.

Adaptive Engineering for Climate Change Joint Strategic Research Centre (AECC)

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A climate warming at a rate faster than scientists have up to this point predicted will require strategies to mitigate, adapt and develop (MAD) focussed at the country, state and municipal levels, since it is at the local level that most national and international goals will be planned for and implemented. During the upcoming Copenhagen Climate Meeting (COP15) politicians will attempt to obtain an agreement on the reduction of greenhouse gases so that the mean global temperature increase remains within a limit of 2 °C. What will this agreement mean for the local level and how will local governments plan for and implement MAD strategies?

Policies to reduce greenhouse gas (GHG) emissions will affect public planning in various ways, for instance through the choices made regarding the transport sector, public transportation and agriculture as well as the selection of fuels and processes for heating. There will be new building codes to improve thermal efficiency, and new planning to ensure sustainable urban development. New business ordinances will likely be developed to ensure prosperity and innovation in the appropriate sectors.

The interdependency of the emission of greenhouse gasses and the emission of other pollutants are not well characterized at either international or national levels, especially with respect to GHG fluxes from land areas that might even exceed urban sources. However, it is clear that the most cost effective abatement is to look at both groups together and to make necessary adjustments as early in the planning and development process as possible.

The deficit in knowledge is even more evident on a local and regional level. It is therefore imperative to give local and regional planners and decision makers the necessary knowledge to optimize both the rural and urban environment with respect to expected increases in the emissions of greenhouse gasses and other pollutants due to a warming climate and to describe the local.

By optimizing their GHG emissions, they optimize their energies as well.

The AECC will establish a technical toolbox based on scientific measurements and studies of the Southern Danish Region and Sønderborg, Denmark with its unique initiatives resulting in practical planning applications for local and regional decision makers to best mitigate, adapt and develop their areas of responsibility given the coming climate change. Leverage from national industrial experts and the Sønderborg initiative ensure a strategic and operational focus for this program. The project is currently under development and first thoughts on the projects are presented at this meeting with the aim of attracting interested international collaborators. The project team already consists of Danish national scientists from relevant research programs as well as relevant public and private partners.

The CESAM Projekt: A New Multiphase Simulation Chamber. Tests and First Experiments

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It is now well established that heterogeneous chemistry has a drastic impact on the composition of the troposphere. The complex physicochemical processes involved in this chemistry which include :phase exchange, surface reactions, reactions in condensed phase followed by transfer to the gas phase have to be quantified in order to be able to develop reliable atmospheric models, and thus have a better understanding of the tropospheric chemistry.

Integrating heterogeneous physicochemical parameters (kinetics constants, accommodation coefficients, etc...) requires to develop new tools allowing to perform experiments in conditions as close as possible to natural ones. This is the goal of the new simulation chamber called CESAM (which means Multiphase Atmospheric Experimental Simulation Chamber).

This simulation chamber has been designed specifically to perform in realistic conditions experiments involving several phases like particulate matter, water droplets, ice crystals, and gas phase. This large volume reaction chamber (approx. 4.2 m^3) is adequate to conduct simulations involving trace concentrations of gas compounds and yet let a long enough life time to the particles. This reaction chamber can be emptied to a vacuum as low as 1.6×10^{-4} mbar which limits the memory effect of the chamber between two experiments. It is equipped with analysis systems allowing the characterization of gas, particulate and aqueous phases. An irradiation system composed of three 4000 W XBO lamps has recently been installed on the top of the chamber and will allow us to reproduce the solar irradiation inside the chamber. 12 ports of 350 mm and 450 mm in diameter are distributed around on the side of CESAM in order to be able to welcome the scientific equipment of other international groups. The location of the chamber in a large technical hall on the ground level makes the site particularly accessible for the installation of other equipment. Large scale experiments involving the expertise of different groups (indispensable to be able to integrate complex heterogeneous processes) will thus be possible. The new chamber can be used as well as an intercalibration platform for different systems dedicated to the study of the physics or the chemistry of the aerosol.