CONTENTS

Foreword
Kulmala M.

EUCAARI WORK PACKAGE ABSTRACTS

1. Emissions and Formation Element

Nucleation (WP 1.1)

Mentel T. F. on behalf of WP1.2 team
Formation and growth of organic particles (WP 1.2)

Anthropogenic and biogenic emissions of aerosols and precursors (WP 1.3)

A model for multicomponent partitioning of semi-volatile aerosol components suitable for use in large-scale models (WP 1.4)

2. Transport and Transformation Element

Laj P. on behalf of WP2.1 Team
Evolution of aerosol properties during transport (WP 2.1)

Satellite retrievals (WP 2.3)
Swietlicki E., Baltensperger U., Kanakidou M., Facchini M.-C., Kiss G., Pio C., Stohl A., and Simpson D.
Regional aerosol source apportionment and long range transport (WP 2.4) .......................................................... 33

Riipinen I., Carslaw K. S., Pandis S. N., Tunved P., Asmi A.
Global/regional-scale particle number – primary vs. secondary, natural vs. anthropogenic (WP 2.5) .......................................................... 36

3. Climate and Air Quality Effects Element

Lohmann U. on behalf of WP3.1 Team
CCN/IN activation and optical properties (WP 3.1) ........................................................................................................... 39

Assessment and quantification of the aerosol indirect climatic effects (WP 3.2) .................................................................................................................. 44

Vignati E., Carslaw K., Brenguier J. L., Kristjansson J. E., Lohmann U., Schaap M., and Kerminen V.-M.
Parameterisations for global and regional models (WP 3.3) .................................................................................................................. 46

Isaksen I., Pandis S., Pilinis C., Hov Ø., and Wolke R.
Regional and global air quality (WP 3.4) .................................................................................................................. 49

Feichter J., Boucher O., Schulz M., Kristjansson J.-E., Iversen T., Kazil J., Kinne S., and O’Donnell D.
Aerosol forcing and climate response (WP 3.5) .................................................................................................................. 51

Boucher O., Carslaw K., Feichter J., Schulz M., Rae J., and Balkanski Y.
Feedback processes and interactions (WP 3.6) .................................................................................................................. 55

4. Integration and Infrastructure Element

Ground site development and aerosol characterization in developing countries (WPs 4.1 and 2.2) ...................................................................... 57
Tunved P., Hansson H.-C., Laj P., Baltensperger U., Krejci R., and Kulmala M. Selection of super sites for Lagrangian studies using special instrumentation and specific questions posed by scientific WPs (WP 4.2) ................................................................. 62

Krejci R. on behalf of WP 4.3, LONGREX, and IMPACT teams Airborne infrastructure – LONGREX and IMPACT intensive observational periods (WP 4.3) ................................................................. 64

5. Impacts Element

Hov Ø., Vignati E., Feichter J., Amann M., and Simpson D. Aerosol impacts on climate and air quality: Integrating into policy (WP 5.1) .............................................................................................................. 70

Burkhart J. F., Stohl A., Tørseth K., Vik A. EUCAARI Platform – Data (WP 5.2) .............................................................................................................. 72

Schulz M., Kinne S., and Tegen I. EUCAARI Platform – Models (WP 5.3) .............................................................................................................. 74

EUCAARI SCIENCE ABSTRACTS

Benkő D., Molnár Á., Imre K. and Párkányi D. Size distribution of total carbon and sulfate concentration in background aerosol, Hungary .............................................................................................................. 80


Carslaw K. S., Spracklen D., and Merikanto J. Evaluating new particle formation mechanisms using a global aerosol model and global CN data .............................................................................................................. 84

Finessi E., Decesari S., Baltensperger U., Mentel T., and Facchini M.-C.
Secondary organic aerosols formation from anthropogenic and biogenic sources: bridging field and smog chamber experiments

Frontoso M. G., Carslaw K. S., Mann G. W., Spracklen D. V., Coe H., Liu D., and Morgan W.
Global aerosol modelling for the intensive LONGREX & IMPACT field campaigns in the framework of EUCAARI project

Frontoso, M. G., Carslaw K. S., Mann G., and Spracklen D. V.
Global aerosol optical properties during the intensive LONGREX & IMPACT field campaigns in the framework of EUCAARI project

Gilardoni S., Vignati E., Cavalli F., Loureiro A., and Artaxo P.
Preliminary results of EUCAARI field campaign in Brazil

Gilardoni S., Vignati E., and Wilson J.
Evaluation tools for black carbon modeling

Gomes L., Burnet F., Schwarzenboeck A., Weigel R., and the ATR-42 Team
Airborne observations of aerosol and cloud properties during EUCAARI intensive campaign with the F-ATR-42

The role of relative humidity in new particle formation

Hoose C., Kristjánsson J. E., Kirkevåg A., Seland Ø, Iversen T., and Storelvmo T.
Sensitivity of cloud droplet number concentration in a GCM to the representation of subgrid-scale vertical velocity

Janhäll S., Andreae M. O., Pöschl U.
Biomass burning fine particle emissions

Kanakidou M., Myriokefalitakis S., Tsigaridis K., Mihalopolos N., Querol X., and Alastuey A.
Natural and anthropogenic contributions to particulate matter in Southern Europe

Kazil J., Quaas J., Kinne S., Rast S., and Feichter J.
Sulfate aerosol nucleation, primary emissions, and cloud radiative forcing in the aerosol-climate model ECHAM5-HAM
Kinne S., and Pöschl U.
CCN climatologies

Lehtipalo, K., Sipilä M., and Kulmala M.
Atmospheric molecular clusters in boreal forest

A model study on growth rates of neutral and charged particles

Cluster and ion spectrometers measuring in 13 EUCAARI field sites

Aerosol mass spectrometric measurements at Cabauw tower during IMPACT May 2008

Merikanto, J., Spracklen D. V., and Carslaw K. S.
Estimating the strength of different mechanisms contributing to the global aerosol budget

Merikanto J., Spracklen D. V., Pringle K., and Carslaw K. S.
Effect of boundary layer nucleation on the change in cloud albedo from 1850 to 2000

Airborne in-situ and lidar measurements of European pollution aerosol properties in May 2008: First results of the DLR Falcon deployment during EUCAARI-LONGREX

Mirme S., Minikin A., and Mirme A.
First high-altitude cluster ion and particle measurements with the NAIS
<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Towards the parameterization of aerosol indirect effects in the large scale models</td>
<td>205</td>
</tr>
<tr>
<td>Modeling aerosol surface chemistry and gas-particle interaction kinetics with K2-SURF: PAH oxidation</td>
<td>209</td>
</tr>
<tr>
<td>Improved boundary layer parametrisation in climate model ECHAM5</td>
<td>211</td>
</tr>
<tr>
<td>Modelling the turbulent mixing and atmospheric particle formation in boundary layer with MALTE</td>
<td>215</td>
</tr>
<tr>
<td>Validation of MODIS aerosol algorithm</td>
<td>217</td>
</tr>
<tr>
<td>New particle formation and aerosol particle characteristics in a semi-clean savanna environment</td>
<td>220</td>
</tr>
<tr>
<td>CCN properties of aerosol particles at SMEAR II in Hyytiälä</td>
<td>225</td>
</tr>
<tr>
<td>Aerosol direct radiative effect from OMI: concept and first result</td>
<td>229</td>
</tr>
<tr>
<td>Tropospheric aerosol chemistry via aerosol mass spectrometry</td>
<td>231</td>
</tr>
<tr>
<td>Overview of the IMPACT campaign at the CESAR site May 2008</td>
<td>234</td>
</tr>
<tr>
<td>Evaporation of mixed inorganic/organic aerosol particles</td>
<td>237</td>
</tr>
</tbody>
</table>
FOREWORD

This is the 2nd EUCAARI Annual meeting abstract book for the European Integrated project on Cloud Climate and Air Quality Interactions (EUCAARI) for the 6th Framework programme of the European Commission. The EUCAARI active period is from 2007 to 2010. The EUCAARI mission is to investigate the effects of aerosol particles on climate and air quality. Quantifying the effect of aerosols on the planet’s radiative balance is one of the most urgent tasks in our efforts to understand future climate change. The uncertainty in aerosol radiative forcing is typically greater than 100%, and for some aerosol components, it is more than 200%, which makes the evaluation of climate sensitivity difficult. Furthermore, the regional scale forcing can be significantly greater than the global average value, as can the associated uncertainties. As a whole, the contributions of the various aerosol sources, the role of long-range transport, and the contribution of primary and secondary particulate matter to the ambient aerosol concentrations over Europe are still largely unknown.

The Objectives of EUCAARI are:
1: Reduction of the current uncertainty of the impact of aerosol particles on climate by 50% and quantification of the relationship between anthropogenic aerosol particles and regional air quality. To achieve this objective EUCAARI will concentrate on the areas of greatest uncertainties and will:
   a. Identify and quantify the processes and sources governing global and regional aerosol concentrations
   b. Quantify the physico-chemical properties of atmospheric aerosols
   c. Quantify the feedback processes that link climate change and atmospheric aerosol concentrations with emphasis on the production and loading of natural aerosols and their precursors
2: Quantification of the side effects of European air quality directives on global and

During the second year of project the intensive observation period (IOP) started in April and it will be finished in April 2009. Over 10 sites around Europe together with EUCAARI sites in China, India, Brazil and South Africa have contributed to the EUCAARI-IOP. In situ airborne obervations were carried out in May 2008 during EUCAARI-IMPACT (Intensive Observation Period at Cabauw Tower) and LONGREX (Long Range Experiment). The preliminary analysis of first IOP results is underway. During the last 12 months remarkable progress in scientific results as well as integration have occurred.

The main fraction of EUCAARI science outcome has been and will be published in the Atmospheric Chemistry and Physics (ACP) EUCAARI special issue. So far 24 papers have been published in ACPD and 15 in ACP in EUCAARI special issue. Ca 95 of EUCAARI deliverables are ready. In this book first set of scientific results together with short work package progress reports are presented.

Finally, I would like to thank all EUCAARI scientists for our progress in joint integrated project.

Helsinki, November 2008

Markku Kulmala, Coordinator
EUCAARI Work Package structure
INTRODUCTION

Work package 1.1 aims at improving our ability to predict the number concentration of new aerosol particles produced via atmospheric nucleation processes. Nucleation is a very non-linear process linked closely to different feedback processes. In large-scale models, nucleation has either not been described at all or is described very crudely. Producing realistic parameterisations of nucleation rates and implementing the parameterisations in large-scale models will considerably improve the present calculations of aerosol impacts on climate and regional air quality. The development and test of cluster spectrometers (ion and neutral clusters) will improve significantly our ability to measure atmospheric nucleation processes. The overall goal of WP 1.1 is to produce parameterized representations of nucleation processes for sulphuric acid – ammonia – water, organic and iodine oxide systems based on combined information from classical nucleation theory (CNT), modelling and experimental studies, to be used in regional and global scale models. WP 1.1 contributes to EUCAARI objectives 1a and 1c as well as to the technical developments.

The specific objectives of Work package 1.1 at the beginning of Year 2 were:

- to calibrate and test the newly-developed air ion and cluster spectrometer under laboratory conditions, and to further develop it to be used in air craft operations
- to conduct homogeneous nucleation experiments for systems involving sulphuric acid, water, ammonia and organic vapours, and to make heterogeneous nucleation experiments for both neutral and ion clusters
- to start the continuous operation of cluster spectrometers, including 2-3 new spectrometers, in 10-12 field sites as part of the EUCAARI intensive observation period.
- to operate and test the new cluster spectrometer in air craft
- to summarize the results of quantum chemical calculations on sulphuric acid-ammonia-water clusters and amine-sulphuric acid clusters, including the effects of ions.
- to test the performance of new calculations and simulations for organo-sulphate-water-ammonia/amine clusters

MAIN RESULTS

The new prototype cluster spectrometer, NAIS (Neutral cluster and Air Ion Spectrometer, see Kulmala et al., 2007), was tested under both laboratory and field condition in Tartu, Estonia. In
laboratory tests, well-defined cluster ions, aerosol ions and neutral aerosol particles were used. The test set-up followed that described by Mirme et al. (2007).

The NAIS was developed further in order to extend its operation to variable altitudes, e.g. airborne operation. The development aimed to the improved control and automatic tuning of air flows and other instrument operation parameters following the variations of ambient conditions. The NAIS was tested in airborne measurements during the EUCAARI long range experiment EUCAARI LONGREX 2008. The NAIS performed very well during the flights. The measurements showed that the aerosol particles and aerosol ions with sizes >2 nm reside in the atmospheric boundary layer up to 2.5 km. At higher altitudes, the number concentration of particles drops down to 100 cm$^{-3}$. The concentration of particles with diameters <10 nm stays in that level up to the height of 11 km and decreases again higher up.

During January–February, 2008, the first (N)AIS calibration and inter-comparison workshop was organised in Helsinki, Finland (Asmi et al., 2008). Ten cluster spectrometers, including four NAIS instruments, were compared and calibrated in the workshop. Calibrations were made with mobility standards and silver particles by using high resolution differential mobility analysers (DMA) and HAUKE-type short DMA. The monomobile mobility standards were measured with the best accuracy. The mobility distribution measured by the (N)AISs broadened to approximately 3 to 5 channels due to the high diffusion of such small ions. Results of the HAUKE and the A/H DMA calibrations overlapped well in the size range 4–10 nm. However, the (N)AISs seemed to detect the ions at about 30-50% smaller sizes compared with the DMA selected sizes. Ion concentrations measured by the NAISs were in good agreement with the concentrations measured by the aerosol electrometer and the CPC. Only at the smallest sizes (>2 nm) the ion spectrometers seemed to overestimate ion concentrations.

Field measurements associated with the EUCAARI Intensive Observation Period were started during the first half of the year 2008. Different type of cluster spectrometers, including 5 new spectrometers (NAIS), started continuous measurements in 13 field sites (Figure 1).

Homogeneous nucleation experiments were conducted using an atmospheric pressure flow-tube and laminar flow tube. Concerning the H$_2$SO$_4$–H$_2$O system, the earlier finding that sulphuric acid generated from a liquid reservoir nucleates much weaker than sulphuric acid generated from the irradiation of sulphur dioxide was confirmed. An explanation to this finding was provided (Berndt et al., 2008). For the H$_2$SO$_4$–H$_2$O-NH$_3$ system, experiments were conducted at different relative humidities (RH) and NH$_3$ concentrations. The prediction of strong enhancement of new particle formation in the presence of NH$_3$ at pptv levels (also for RH up to 100%) given by Coffman and Hegg (1995) are not supported by our experiments. Extrapolation of our results down to NH$_3$ concentrations used by Ball et al. (1999) of 2.0–4.2×10$^9$ molecules cm$^{-3}$ (0.08–0.17 ppb) point to a negligible influence of NH$_3$ for nucleation, being in clear contradiction to the conclusions given by Ball et al. (1999).

A summary on the use of quantum chemical methods in studies of sulphuric acid-related nucleation mechanisms (mainly binary sulphuric acid–water and ternary sulphuric acid–water–ammonia nucleation) was written and published (Kurtén and Vehkamäki, 2008).

The role of ammonia in sulphuric acid–water nucleation was revealed by a series of quantum chemical calculations. As indicated by experimental investigations, ammonia significantly assists the growth of clusters in the sulphuric acid - co-ordinate. Our calculations (Kurtén et al., 2007a;
Torpo et al., 2007) predict that in atmospheric conditions, this effect becomes important as the number of acid molecules in clusters increases from two to three. On the other hand, small molecular clusters are unlikely to contain more than one ammonia molecule per one sulphuric acid (Kurtén et al., 2007b). This implies that the average NH$_3$:H$_2$SO$_4$ mole ratio of small molecular clusters in atmospheric conditions is likely to be between 1:3 and 1:1. Further calculations (Ortega et al., 2008) show that while ammonia enhances the nucleation of neutral sulphuric acid–water clusters moderately effectively, it has little or no effect on ion-induced sulphuric acid–water nucleation. In contrast, short-chain alipathic amines are likely (Kurtén et al., 2008) to enhance both neutral and ion-induced sulphuric acid–water nucleation very effectively despite their low atmospheric concentrations.

Calculations of thermodynamic and kinetic parameters for the reaction of stabilized Criegee Intermediates with sulphuric acid (Kurtén et al., 2007c) demonstrate that quantum chemistry is a powerful tool for investigating chemically complicated nucleation mechanisms which cannot easily be treated with any other simulation methods. The calculations indicate that if the biogenic Criegee Intermediates have sufficiently long lifetime in atmospheric conditions, the studied reaction may be an important source of nucleation precursors. Organo-sulphates formed from the reaction of a variety of terpene oxidation products with sulphuric acid have also been shown to bind very strongly to both each other and to sulphuric acid molecules, indicating that they would be effective nucleation precursors. Organosulfate ions might possibly also play a role in ion-induced nucleation. Concentration measurements and kinetic data on the formation rates of organo-sulphates in atmospheric conditions is needed before further conclusions can be drawn.

**FUTURE PLANS**

The main task of the third EUCAARI year in WP1.1 is to complete the ion spectrometer measurements associated with the Intensive Observation Period (IOP) by May 2009. A data set based on these measurements will be constructed.

A new modelling tool (Ion-UHMA) to assist the interpretation of cluster spectrometer measurements will be developed and tested. The model will be applied to measured ion spectrometer data.

Final results from the conducted nucleation experiments and quantum chemical calculations regarding various organo-sulfate-water-ammonia/amine cluster systems will be published and reported.
Figure 1. Locations of the sites operating cluster spectrometers during the EUCAARI Intensive Observation period.

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WP1.2 FORMATION AND GROWTH OF ORGANIC PARTICLES

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Keywords: SOA formation, SOA yields, SOA markers, ageing process

INTRODUCTION

Biogenic secondary organic aerosols may play an increasing role under future climate conditions. Vegetation models predict an about 50% increase in emissions of biogenic volatile compounds (BVOC) in a warmer climate (Lathiere et al. 2005) and possibly a more than twofold increase of the biogenic SOA burden (Tsigaridis and Kanakidou 2007). From the current point of view, such an increase in SOA could have a cooling potential of the order of 1 W/m², thus constituting a considerable negative feedback between vegetation and climate (Kulmala et al. 2004). Moreover, organics seem to play a pivotal role in new particle formation (Laaksonen et al. 2008). However, despite of this potential importance, today’s SOA sources are highly uncertain and in predicting SOA mass models often fall short by more than an order of magnitude. Bottom-up estimates, extrapolating data from laboratory oxidation experiments, give total biogenic SOA fluxes of 9-50 TgC/yr (Kanakidou et al., 2005). Recent top-down inverse estimates give higher estimates for SOA, with a broad range from 140 – 910 TgC/yr (Goldstein and Galbally, 2007). The discrepancy could be due to missing precursors (e.g. Robinson et al. 2007) or missing long term chemistry in the laboratory studies. WP.1.2. addressed SOA formation by using real plants as VOC emission sources (Task.1.2.1), making long term photochemical simulation studies (Task 1.2.2) and searching for new chemical pathways and mechanisms of multi-phase oxidation (Task 1.2.3). The synthesis of the results of the Tasks 1.2.1.- 1.2.3 will by the modelling Task .1.2.4.

EXPERIMENTS

Experiments were performed in the plant chamber (Task 1.2.1) and the SAPHIR chamber (Task 1.2.2) at FZJ (24). In these simulation experiments we applied a multi-methodological approach in gas-phase (including measurement of OH radicals) and particulate-phase measurements. This included on-site cooperation between the partners comprising aerosol microphysical characterization, aerosol mass spectrometry, and chemical analysis of filter samples. Three plant chamber campaigns (total of 6 month) and two SAPHIR chamber campaigns under autumn and summer conditions (total of 2.5 month) were successfully accomplished. The data are currently under evaluation. The partners in Task 1.2.3 provided detailed studies of ageing processes applying an aerosol chamber (IfT (4)), flow tubes, and contact angle measurements (PSI (19), CNRS (2)). Partners PSI and CNRS focussed in detailed experiments i) on the effect of the photosensitized uptake of O₃ to organic films on the substrate’s hydrophilicity; ii) the quenching kinetics of a model photosensitizer in aqueous solutions; and iii) the extent of photosensitized polymerization of dicarboxylic acids in an aerosol.
RESULTS

The plant chamber experiments in Task 1.2.3 focussed on species of the Boreal forest. We observed simple linear relationships between the carbon mixing ratio of monoterpenes & sesquiterpenes and formation rate of 3 nm particles, condensational growth rate, and SOA mass. The slope of the latter agrees with the analysis of field observations in the Boreal forest by Tunved et al. 2008 (Fig.1). The results in principle allow to construct the SOA formation of a forestal system from the tree species. By using our observed SOA formation efficiencies weighted by the abundance of tree species in the Boreal region around Hyytiälä, and the mass of pre-existing aerosol by Tunved et al, we predict a SOA mass within 6% for todays situation. Similarly, by linear extrapolation we predict a future SOA increase of about 20% for a 50% (climate-induced) increase of Boreal MT and SQT.

In the campaigns in the SAPHIR chamber in Task 1.2.2 the partners investigated a mix of those MT and SQT which are main components of tree emissions of Boreal species. This was supposed to create the link to Task 1.2.1 and to field studies in Hyytiälä. The experiments were performed under low NOX regime and at various actinic fluxes (autumn - summer, cloudy - sunny). Particles were formed during the first day and than aged over a second day. OH radicals and ozone served as oxidants; experiments at low actinic fluxes were dominated by ozone oxidation, whereas oxidation by OH radicals dominated at high actinic fluxes. The total VOC precursor concentration and the presence of SQT served as further variables. As key quantities the particle composition, the particle size and mass distribution, hygroscopic growth, CCN activity, and volatility were measured. Moreover, OH radical concentration was measured in most cases. This will allow to calculate the OH dose seen by the aerosols and to correlate it with the progress of chemical ageing reactions. Chemical ageing of particles was detected by on-line APCI mass spectrometry and in the analysis of filter samples by H-NMR spectroscopy and various LC-MS techniques. Marker compounds for chemical ageing were detected by APCI-MS, CE-MS, LC-ESI-MS as well as GC-MS. Figure 2 compares APCI-MS results of fresh SAPHIR, PSI chamber, aged SPAHIR, and Hyytiälä data. The marker composition of the aged aerosol approaches the pattern observed in Hyytiälä, however with an excess of ozonolysis products.
OC analysis in aerosol water extracts with respect to total OC indicate that the water soluble fraction increases upon chemical ageing (Fig. 3). HNMR analysis shows the decrease in content of first-generation degradation products such as pinonic acid in aged SOA samples. In the autumn data no significant chemical formation of HULIS was observed on the time scale of two days.

In general the microphysical properties of particles reflected the changes in particle composition by the ageing processes, but dramatic changes were not observed. The most important parameter influencing microphysical properties was actinic flux / OH oxidation, whereby sunny days favour the formation of more hygroscopic particles and OH radicals seem to be needed to make chemical ageing manifest in hygroscopic properties. As can be seen from these selected and partially preliminary results the partners provided a comprehensive data set of SOA formation with promising results regarding chemical ageing, SOA marker compounds, and microphysical properties of the resulting aerosols.

In Task 1.2.3 heterogeneous reactions were studied between organic films and ozone in presence of simulated sunlight and the photosensitizer 4-carboxybenzophenone (4-CB). Films of oxygenated aromatic
compounds were taken as proxies for atmospheric aerosols. Depending on the film substrate the photosensitized reaction with ozone lead to more hydrophobic surfaces as monitored by contact angle during the reaction (Figure 4). Such behavior indicates that photo-induced aging processes involving ozone (such as oligomerisation) not necessarily favour increased hygroscopicity of organic aerosols in the atmosphere. The reactivity of mixtures of the photosensitizer benzophenone with large excess of dicarboxylic acids was investigated. In the presence of organic acids, the triplet state of benzophenone is quenched, and a new species is formed. Possibly, such reactive quenching interactions could provide the initialization of oligomerization in the atmosphere. A model aerosol consisting of ammonium sulphate, benzophenone and dicarboxylic acids was exposed to light in a irradiated aerosol flow reactor. By CIMS a decay of adipic acid in favour of a mass fragment with m/z of 293 was detected, whereas a shift of the m/z 43/44 ratio was observed by WToF-AMS.

![Figure 4](image-url)  
**Figure 4.** Change of the contact angle with the time of ozone and light exposure for the solid organic film 4-CB/4-phenoxyphenol

**SUMMARY AND STATUS OF WP1.2**

According to the planning WP1.2 ends at the end of year two. The experiments needed to achieve the goals were successfully performed in close interaction between the partners. Evaluation is currently under progress. Preliminary and available data indicate that the observation of SOA formation from tree emissions can possibly lead to simple parameterizations for models in order to predict future SOA formation and microphysical properties of the particles. Photochemical aging of biogenic SOA is happening under natural oxidant and light conditions on time scales of one day. It could be observed in the SAPHIR chamber by online aerosol mass spectrometry as well as by offline methods (LC-ESI/MS) and marker compounds could be identified. The concentrations of marker compounds can be used to determine the photochemical age (i.e. the “age spectrum”) of biogenic SOA. Moreover, valuable quantitative information on the time scale of oxidative processing, i.e. kinetic data for implementation into models can be extracted. Photochemical aging changes chemical composition and thus the microphysical properties of SOA particles, its manifestation depends on oxidation regime during the formation and ageing process. Photoenhancement of ozone reactions at particle surfaces possibly leads to initialization of oligomerization processes. This process can make surfaces more hydrophobic. The partners still need some time to fully develop the potential of the gathered experimental data for identification and quantification of processes of formation and chemical aging of secondary organic aerosols.

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EUCAARI WP 1.3:
Anthropogenic and biogenic emissions of aerosols and precursors

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Abstract
EUCAARI WP 1.3 aims to deliver inventories of anthropogenic and biogenic (primary) emissions of aerosols and precursors to be used in air quality and climate models models within EUCAARI. Furthermore, a first number-based emission inventory will be produced as input for models to answer a series of questions raised in EUCAARI. To fulfil these aims, tasks were split among the partners in WP 1.3 to cover natural sources, anthropogenic carbonaceous aerosol emissions and gap-fill any holes in particle number emission factors for key sources such as biomass burning, residential wood combustion and transport. Moreover, considerable effort went into a more accurate spatial distribution of emissions through updating point sources, road transport maps, land use maps and residential wood use. Since particle numbers unlike mparticle mass are not a stable entity the WP developed a number-emissions pre-processor for Chemical Transport Models that parameterizes the particle number emissions to the model scale. An improved mass-based Pan-European emission inventories of primary carbonaceous aerosols is currently available for use in other EUCAARI WPs.

1.1 Methodological developments

1.1.1 Parameterizing the effect of sub-grid scale aerosol dynamics on aerosol number emission rates
The method calculates the probability that a given particle emitted inside the grid cell will survive and be available for transfer outside the cell. This survival probability is calculated theoretically as a function of the emitted particle size and the pre-existing aerosol size and the residence time in the grid cell. The net number of particles effectively emitted to the grid cell can then be calculated by multiplying the size dependent emission rate in the inventory with this survival probability function. The method simultaneously conserves mass by adding the mass of particles lost by coagulation to the larger particle sizes. The approach is grid-size independent and can be used in models of all scales. It is described in more detail by Pierce et al. (2007).
1.1.2 Spatial distribution of Emissions

In 2008 TNO updated and “overhauled” its European point source data used for gridding and distributing emissions. Also new distribution maps for e.g. animal husbandry, road transport and residential combustion were made. Some examples of these distribution maps will be given. The maps can be used to distribute e.g., emissions of particulate matter, precursors, carbonaceous aerosols and particle numbers.

1.2 Particle numbers and fluxes from natural sources.

The mains sources to be considered in this category are marine aerosols, forests and vegetation or biomass burning. As the processes influencing the emissions are mostly driven by climate the emissions may vary widely from year to year as well as within the year. This asks for a different approach than anthropogenic emissions which are mostly driven by activities and their respective technological level.

1.2.1 Fluxes from forests

An evaluation of the importance of upward fluxes of particles over European forests has been made by Pryor et al. (2007). Forests are net sinks for particle mass and number but we are trying to quantify the frequency with which upward fluxes are observed and the mechanisms that generated those upward fluxes. Such processes may include non-local turbulence and particle dynamics (including nucleation) at/near the canopy.

1.2.2 Marine aerosol particle number fluxes

Global and Regional submicron sea spray fluxes, in terms of both number and mass and organic fraction were produced for the year 2006 (MAP, 2007). The output in the form of marine particle number flux maps needs to be validated with observational marine particle flux data. Therefore, data from the Galathea global cruise and MAPIT observations were analyzed. The main research questions are 1) Optimal methods for particle number flux estimation (corrections for ship motion, use of dissipation method) and 2) Evaluation of existing particle number flux algorithms incl. wind speed and Sea Surface Temperature (SST) dependence. Results to date (research ongoing) show a good operationalization of dissipation method and new method for computing uncertainty bounds on the PN flux. However, particle number fluxes from Galathea are an order of magnitude higher than from MAPIT project. The cause of this observation is uncertain and demands further study.

1.2.3 Particle number emissions from biomass burning

Biomass burning is a somewhat different semi-natural source as most fires are somehow linked to human activities or presence. Over the past year the available literature and data of particle number emission from biomass burning has been screened and summarized in an overview which will be presented by Janhäll et al. (2008). This results in advised emission factors for PN emissions from biomass burning.

1.3 Anthropogenic particle number inventory

The production of an anthropogenic particle number inventory is a difficult endeavor due to several complications e.g.; measurement of particle number emissions are not standardized and may start at various sizes. The emission factor describing the total number of particles emitted from the same source will vary widely if PN from 10 nm are included instead of only from e.g., 30 nm and up. Measurements in the smaller size ranges are often mobility diameter as opposed to aerodynamic diameter for the larger size particles; again conversion of one to another is complicated. Last but not least, for some sources particle number emission data are simply lacking. To be able to make progress a pragmatic approach is taken where we focus on covering the key sources and estimating the remaining smaller sources by converting particle
mass to particle numbers using more general particle number distribution data. The progress for some of the major sources will be discussed most notably:

- A literature review of particle number size resolved emission factors for biomass combustion in residential appliances (fireplaces, stoves and boilers) which showed that for this important source a (surprisingly) rather consistent results emerges regarding emission factors and size distribution of emissions.
- Compilation of PN emission factors for stationary combustion sources such as coal fired power plants.
- Road transport is one of the other most important sources of PN (Denier van der Gon et al., 2007). Our PN inventory for this source will build upon data from the EU PARTICULATES project (Ntziachristos et al, 2004; Thompson, 2004). Within the WP emission factors for the sources not covered by PARTICULATES were made.

1.4 Carbonaceous aerosols

A new European inventory of EC and OC for 2005 has been made based on previous data (e.g. Bond et al. 2004; Streets et al. 2001) and data from IIASA’s RAINS and GAINS PM inventories (Klimont et al. 2002, Kupiainen et al. 2004); As a partner to EUCAARI IIASA collaborated closely with WP 1.3 and made their latest data available (pers comm.. Z. Klimont ). The distribution of the EC and OC emissions is based on the work done by TNO in the framework of the PAREST project [Denier van der Gon et al. 2008, work in progress]. Results of the EC and OC inventory will be presented. For example figure 1 illustrates that total organic matter for several source categories is the most important component for mass closure in PM2.5 but that this may vary highly by source category. Total carbonaceous aerosol (TC) for Europe in 2005 amounts to ~2000 kt/yr of which ~10% is due to international shipping.

![Figure 1 Example of result form the OC inventory: Emission of Organic matter versus PM2.5 for Europe in 2005 by source sector](image)

 Independently calculation of ratios OC/EC/TC/CO to NOx for a traffic source using field data have been made. Ratios have been calculated to account for diurnal, weekday/ weekend and seasonal variations. These results may be used to further improve the EC/OC inventory.
1.5 Future outlook

In the next months the reviews of particle number emission factors for various sources will be finalized. Next we will compile our first PN inventory. After this special attention will be given to making an overview of all WP 1.3 products and publishing the findings and results of this WP. After some of the products have been used within EUCAARI a task will be to evaluate the accuracy and optimization of the inventories involving all WP partners and feedback from other WPs.

Acknowledgment

As a partner to EUCAARI IIASA (Klimont et al.) collaborated closely with WP 1.3 and made their latest data available for use in the EC/OC inventory.

References


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A MODEL FOR MULTICOMPONENT PARTITIONING OF SEMI-VOLATILE AEROSOL COMPONENTS SUITABLE FOR USE IN LARGE-SCALE MODELS

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Keywords: Secondary aerosol, partitioning, multicomponent, organic, thermodynamics.

AIMS

To develop code to account for the partitioning of semi-volatile components in the atmosphere accounting for the presence of inorganic and organic primary and secondary components

INTRODUCTION

Semi-volatile compound partitioning from the gas phase to atmospheric aerosol particles is thought to be a major driver in secondary aerosol mass formation. Inorganic component partitioning is thought to be relatively well understood, but models attempting to explain the mass of organic material using absorptive partitioning, deriving the required parameters can be derived from first principles, systematically underpredict ambient aerosol mass loading. Models with partitioning coefficients tuned to fit chamber data, whilst seldom fitting ambient measurements may be tuned or modified to suit. The aim of this work is to deliver a partitioning module, based on our best scientific understanding that is sufficiently efficient and stable to be used in larger scale models including a realistic representation of organic aerosol components. The module should be accurate and sufficiently flexible to include all atmospherically important components and processes.

METHODS and RESULTS

WP 1.4.3: The non-iterative partitioning framework has been specified and takes as input the components in the aerosol, the ambient temperature and RH and outputs the vapour pressure of all semi-volatile components and the water content of the aerosol corresponding to the composition. The scheme does not separate the broad aerosol composition space into discrete regions of applicability unlike other approaches. The scheme includes major inorganic semi-volatile and involatile electrolytes and for these components is more accurate (using AIM as a benchmark) for the vapour pressures of NH₃, HCl and HNO₃ than the comparable MTEM model (Zaveri et al., 2005) and uses less CPU time per calculation. Water content prediction uses a comparable calculation and is almost identical in accuracy, but is more efficient. The construction of the partitioning module and its incorporation into an aerosol dynamics model, demonstrating its suitability for a number of applications has been described in a manuscript which has been modified for publication after initial peer review (Topping et al., 2008).
WP 1.4.2: In parallel to the construction of the partitioning framework, a number of simulations using the Master Chemical Mechanism (MCM) for atmospheric oxidation have been conducted. The input conditions for the simulations are based on the UK NAEI detailed high resolution emission inventory and measurements from a polluted continental field project (TORCH), downwind of London in 2003. The emission scenario has been varied to change the ratio of anthropogenic to biogenic VOCs (as well as scaling the NOx by the same factor). Predictions of the vapour pressures of around 3500 predicted components have been made using a number of techniques, improving the techniques for compounds for which there is a reliable basis set of laboratory-determined vapour pressures. These vapour pressures have been included in a modified mole fraction-based (as opposed to mass fraction-based) absorptive partitioning scheme to predict the speciation and total mass of secondary organic material formed from the oxidation products in each scenario. The modified absorptive partitioning scheme allows the impacts of variable RH on the organic speciation and total mass to be investigated. This method is the subject of a manuscript in open peer-review (Barley et al., 2008). The organic compounds across all scenarios have been ranked according to their abundance in the predicted total SOA mass and selected as the semi-volatile organic components to be used in the EUCAARI multicomponent partitioning module. The conditions (temperature, dewpoint and core required to attain a range of target aerosol mass formed) for the simulations have been varied systematically to explore the sensitivity of the rank-ordering.

Figure 1: The distribution of predicted organic compounds in terms of their Oxygen / Carbon ratio and molar mass for anthropogenically- (left panels) and biogenically- (right panels) dominated simulations, allowing (top panels) and prohibiting (bottom panels) anhydride hydrolysis. The symbols denote observed atmospheric compounds.

Vapour pressure determination for malonic, succinic, glutaric and adipic acids have been made, in addition to vapour pressure determinations in ternary mixtures including involatile inorganic components (NaCl). Furthermore, the vapour pressures of a range of multifunctional compounds are ongoing.
WP 1.4.1 and 1.4.4: The framework into which the inorganic electrolytes have been included has been extended to include semi-volatile and involatile organic components. The semi-volatile compounds have been selected as described above: 10 deriving from biogenic precursors, 3 from anthropogenics. The partitioning module has been compared directly against predictions (for vapour pressure and water content) made using a benchmark thermodynamic code developed at the University of East Anglia and released online as E-AIM. This has been possible for all systems (far wider than originally envisaged owing to the far greater flexibility of the benchmark code. The involatile compounds in the partitioning code are currently loosely defined. It is likely that they will be represented by two macromolecular functional entities, one polyfunctional acidic, the other a polyfunctional neutral compound. At present, they are loosely based on an average broad functionality derived from a variety of field measurements and have been used in deriving the thermodynamic fits to calculate the water content and vapour pressures of other components. Currently there is no description for the formation mechanism for these macromolecular compounds and their mole fraction is an argument to the sub-routine. It is likely that condensed-phase accretion reactions play a significant role in their formation and in the increasing mass beyond that predicted by equilibrium or simple disequilibrium partitioning. It is relatively straightforward to include such reactions should their rates and product yields become available (from EUCAARI or elsewhere) throughout the development cycle of the module.

FUTURE DEVELOPMENTS

There are several developments which will take place over the forthcoming period:
i) the vapour pressure predictive techniques, as far as possible, will take into account the vapour pressures derived from evaporation measurements at the University of Copenhagen. Little acids formation is predicted from gas phase oxidation and the degree to which the measurements will improve the partitioning module will be investigated. However, it is expected that vapour pressure determinations for multifunctional compounds will become available and these will be used to evaluate the more complex vapour pressure prediction techniques.

ii) the semi-volatile, and in particular the involatile, organic component representation will be refined in response to a broader range of analytical characterisations from multiple locations, including the EUCAARI field measurements; such measurements should have been

iii) chamber and laboratory experiments, both within EUCAARI and outside EUCAARI will be used to inform the module to allow more realistic representation of condensed phase accretion reactions and to evaluate the predictions made using the simple disequilibrium mass transfer processes included to-date.

iv) the reduced gas phase oxidative mechanism currently favoured to be coupled to the partitioning module will be fully evaluated and further developments and modifications assessed

v) it has been postulated that components that are conventionally considered to be part of the primary emissions of motor vehicles may evaporate into the gas phase in the diluting exhaust, repartitioning once they have been oxidised to sufficiently reduce their volatility. The ability of oxidative degradation mechanisms to represent the degradation of these components will be investigated.

vi) condensed phase reactions are likely to play a role in the condensation of organic components by removing semi-volatile compounds in the condensed phase, hence reducing their vapour pressure. The means to realistically incorporate a mechanistic description of such reactions will be explored.

REFERENCES


27
WP 2.1 EVOLUTION OF AEROSOL PROPERTIES DURING TRANSPORT

Work package leader: Paolo Laj

WP 2.1 will quantify the evolution of aerosol properties, particularly aerosol mixing state and hygroscopic growth factor upon transport in the Boundary Layer or Lower Free Troposphere. This will be performed by i) direct continuous observation of aerosol mixing state, hygroscopic growth and size segregated chemistry in addition to standard EUSAAR measurements coupled with back-trajectory analyses and ii) intensive observation periods following the evolution of aerosol properties on a temporal scale of 1-3 days.

Aerosols and clouds play an important role in the radiative budget of the atmosphere, through both direct scattering effects and indirectly through perturbations of the cloud fields. The knowledge of bulk chemical composition and size distribution alone is not sufficient to predict aerosol hygroscopic growth. One of the most important factors controlling the ability of particles to absorb water is the degree of mixing of the aerosol population. The chemical mixing describes to what extent the different components are existing on each and every particle. An aerosol is called internally mixed when all particles have the same chemical composition. Nearly all models developed to date have assumed that the aerosol is "internally mixed", that is that all particles of the same size have the same chemical composition. We know from recent field campaigns that this is not true, especially closer to emission sources.

Simultaneous long-term measurements of the aerosol size distribution, hygroscopic growth and size segregated chemical characterization are theoretically sufficient to estimate the fraction of aerosol particles activated at a given supersaturation, and also the processes responsible for the aerosol evolution. This relationship is, at present, either derived from semi-empirical relationships between aerosol mass or number and cloud droplet concentration or by prognostic relationships between CN and supersaturation of water vapour. Both approaches commonly tend to overestimate droplet number concentration and do not consider possible artefacts such as the presence of soluble gases or organic material on aerosol particles.

List of WP 2.1 tasks:
Task 2.1.1 Continuous monitoring of aerosol properties in Europe
Task 2.1.2 Size-segregated chemistry and CCN properties
Task 2.1.3 Lagrangian experiment
Task 2.1.4 Analysis and processing of Lagragian and continuous measurement data
INTRODUCTION

Optical instruments on satellites, i.e. radiometers and spectrometers, are used to retrieve aerosol and cloud properties over large spatial scales. Most of the satellites used are in a polar orbit (MODIS, POLDER, OMI, AATSR) and provide daily snapshots during the time of overpass. The area observed depends on the swath. Instruments such as OMI, POLDER and MODIS provide (near) global coverage, AATSR has a revisit time of three days at mid-latitudes. SEVIRI, on the other hand, flies on MSG in a geostationary orbit and provides data every 15 minutes.

In the second year of EUCAARI, the satellite retrieval work in WP2.3 has focused on providing data contributing to the EUCAARI field campaigns LONGREX and IMPACT. The DLR Falcon flew during these campaigns as well, providing in situ measurements complimentary to the satellite measurements.

AEROSOL RETRIEVAL

Aerosol products include the total aerosol optical depth (AOD) from MODIS, OMI and AATSR, and fine mode AOD from POLDER. These products are available for every day during the campaign, for cloud free conditions. In the presence of clouds, aerosol retrieval is not possible. The daily products have been used to provide monthly composite aerosol fields. In addition CALIPSO L1 and L2 products are available.

As an example, the total AOD over Europe for 14 May, 2008, retrieved using MODIS/TERRA, AATSR and OMI are presented in Figure 1, together with the fine mode AOD from POLDER. The POLDER retrieval uses the polarization capability of the sensor. Large particles are not sensitive to polarization and hence only fine mode AOD is retrieved, which is lower than total AOD. AOD patterns from MODIS, AATSR and POLDER are similar for the areas for which data from all three sensors are available, although some differences are observed as well. All three sensors use their own cloud screening and retrieval method.
MODIS and POLDER show regions of enhanced AOD south of Ireland which are qualitatively in agreement with CALIOP lidar extinction profiles. The DLR Falcon flew in the same area on 14 May and also observed very high extinction.

The combined in situ and satellite data sets can be used for further evaluation of the aerosol properties during the campaigns.

![Figure 1](image1.png)

Figure 1. AOD retrieved using different instruments, for 14 May 2000: (a) MODIS/TERRA AOD (scale 0-0.4) at 550 nm; (b) POLDER/PARASOL fine mode AOD at 550 nm (0-0.3); (c) AATSR AOD at 555 nm (0-0.7); (d) OMI AOD (0-3.0). Note the different AOD scales (see colour bars).

**CLOUD RETRIEVAL**

Cloud properties are available from MODIS (TERRA: 10:30 local; AQUA (14:30 local), POLDER, OMI and SEVIRI. OMI cloud products include the effective cloud fraction and the cloud pressure retrieved using the oxygen dimer (O$_2$-O$_2$) absorption band around 475 nm. The products available from MODIS and POLDER pixel level retrievals and daily, weekly or monthly gridded level 3 products. The most relevant cloud properties from these instruments are cloud fraction, cloud phase, optical depth, effective radius, liquid water path, cloud top pressure and short wave albedo. As an example, cloud cover, cloud phase, cloud top pressure, cloud optical depth and SW albedo for 14 May, retrieved from POLDER/PARASOL, are presented in Figure 2.

Figure 3 shows an example of an MSG SEVIRI retrieval for 14 May. The different colours are associated with the reflectance in different wavebands and hence provide information on the aerosol microphysical properties.
CONCLUSION

Satellite products are available for the EUCAARI campaigns LONGREX and IMPACT. MODIS, POLDER and OMI provide both aerosol and cloud products. MSG SEVIRI provides information on the cloud microphysical properties with high temporal resolution. AATSR provides information on aerosol optical depth. Extinction profiles for the CALIPSO overpasses are available as well as data from the DLR FALCON using lidar and in situ measurements.
These data need to be further evaluated and interpreted through intercomparison of satellite products and comparison with in situ measurements using both aircraft and ground-based data. Satellite data need to be validated versus available AERONET data.

The use of OMI data, together with ground-based data from the IMPACT campaign in Cabauw, to estimate the aerosol direct radiative effect is presented in Veihelmann et al.

REFERENCES

INTRODUCTION

WP 2.4 aims at improving our ability to accurately apportion the European aerosol to its various sources. The focus will be apportionment of aerosol mass (PM), with special attention to the development and implementation of new methodologies for source apportionment of the organic aerosol components. The aerosol source apportionment will distinguish between anthropogenic and natural, as well as primary and secondary aerosol components. WP 2.4 will develop tools that will enable a quantitative estimate of the influence of various sources to the AQ and PM levels within Europe, in particular regarding the organic aerosol. WP 2.4 contributes to the EUCAARI objective 1a.

More specific objectives in WP 2.4 are to produce

- Source apportionments of the organic aerosol at European sites (Task 2.4.1)
- Determine the geographical source region (Task 2.4.2)
- Updated EMEP model for the concentration fields of mineral dust and sea salt (Task 2.4.3)
- Organic aerosol (OA) process description and parameterization (Task 2.4.4)

ONGOING AND FUTURE WORK

The activities of WP 2.4 are still ongoing.

Task 2.4.1
The aim of this Task is to perform a source apportionment of the organic aerosol at selected European sites by means of source-specific tracer compounds quantified using various analytical techniques:

- GC-MS Molecular tracers (Task 2.4.1a, Partners UAV and ACUV)
- H-NMR spectral fingerprints (Task 2.4.1b, Partner CNR-ISAC)
- AMS spectral fingerprints (Task 2.4.1b, Partners LU and PSI)
- $^{13}$C (Task 2.4.1c, Partners LU and PSI)
Details on the various analytical techniques can be found in EUCAARI Deliverable 9 (Initial implementation strategy and prioritize tasks in the workplan for WP2.4).

OA source apportionments are performed at six background sites. Five of these are EUCAARI-EUSAAR sites, while one site (San Pietro Capofiume) is operated by one of the EUCAARI-EUSAAR partners (CNR-ISAC). Three of the sites participated in the Lagrangian experiments (Hyytiälä, Melpitz, K-puszta). Additional background sites are San Pietro Capofiume, Finokalia and Montseny. Urban sites where OA source apportionment will be performed are Zürich and Barcelona. More details on the selection of sampling sites can be found in EUCAARI Deliverable 32 (Selection of sampling sites, coordinated with WP 2.1, 4.2 and EUSAAR). OA sampling has already been performed at Hyytiälä, Finokalia, San Pietro Capofiume, Meplitz and K-puszta, while sampling at Barcelona/Monseny, Zürich and again Hyytiälä will be done in the first half of 2009.

Since funding is very limited within EUCAARI for the source apportionment task, we are forced to focus on shorter and more intensive campaigns rather than long-term measurements, which would have otherwise been beneficial for OA model validation. This is however compensated by the use of a several source apportionment methodologies which, when combined in time and space, will provide deeper insight regarding the sources contributing to the OA concentrations.

The selection and analysis of OA samples using GC-MS, H-NMR and $^{14}$C is currently ongoing.

At the AMS (Aerosol Mass Spectrometry) User’s Meeting in Manchester (UMAN) in September 2008, eight AMS users agreed on a coordinated effort to deploy their AMS instruments at various background sites in Europe during the two EMEP intensive OA campaigns in September-October 2008 and February-March 2009. The AMS turnout within the community is certainly excellent considering the limited number of AMS instruments available in Europe. Many of the instruments are of the high-resolution type w-ToF-AMS, enabling quantitative analysis of oxygenated OA (OOA) and hydrocarbon-like OA (HOA), as well as tracer m/z peaks that are characteristic for biomass combustion (e.g. levoglucosan). EUSAAR/EUCARI background sites operating AMS instruments include Harwell, Hyytiälä, K-puszta, Mace Head, Melpitz, Puy de Dôme and Vavihill. In February-March 2009, AMS will also be deployed at Cabauw and Montseny. Data processing workshops will be arranged within the EUCAARI-AMS community to ensure data quality and intercomparability between sites.

An intercalibration (round-robin test) will be carried out within the European $^{14}$C analytical community, including WP2.4 partners PSI-ETHZ and LU. Samples from the EUCAARI/EMEP campaigns will be analyzed for $^{14}$C by PSI-ETHZ and LU. At LU, the separation and graphitization scheme of OC/EC for subsequent $^{14}$C analysis has been developed in cooperation with PSI-ETHZ, and intercomparison tests will be performed.

Task 2.4.2
FLEXPART calculations have been performed by NILU for all EUCAARI/EUSAAR sites and are continuously being updated. These will be used to determine the geographical source regions. The FLEXPART output data are presented at http://transport.nilu.no/projects/eucaari.

Task 2.4.3
Updates of the EMEP model for the concentration fields of mineral dust and sea salt is carried out within EMEP MSC-W, and ongoing.

Task 2.4.4
This task aims to evaluate the uncertainties in the formation and fate of secondary organic aerosol (SOA) in regional and global models, and develop improved parameterizations. These uncertainties in the SOA component simulations are associated with a number of adopted simplifications in order to reduce the
computational requirements of the modules. The evaluation of the simulations is performed by comparison with observational data. 

As a first step to the evaluation and subsequent improvement of the organic aerosol component (OA) simulations in the EUCAARI models, the EMEP and the ECPL model parameterisations of secondary organic aerosol (SOA) formation in the troposphere have been compared, differences have been identified and critical gaps in knowledge have been pointed out. The update of the model parameterizations to the recently published kinetic and yield data is ongoing and will be evaluated during the next phases of the project.
GLOBAL/REGIONAL-SCALE PARTICLE NUMBER – PRIMARY VS. SECONDARY, NATURAL VS. ANTHROPOGENIC: WORK PACKAGE 2.5

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Keywords: Models, global, regional, particle number, primary, secondary, natural, anthropogenic

INTRODUCTION

Work Package 2.5 aims to quantify the relative contribution of natural and anthropogenic as well as primary and secondary sources to particle number concentrations at climate-relevant sizes. The budget of particle number concentration is essentially unknown except in specific environments with a few dominant sources (such as urban areas). Directly emitted (primary) particles contribute directly to particle number, and natural and anthropogenic emissions of gases, such as SO\textsubscript{2} and organics, can lead to formation of new (secondary) particles through their nucleation and condensation. We need to know what fraction of particles comes from primary particles and what fraction is formed through nucleation in different environments. Without such fundamental information, long-term changes in aerosol abundance, and hence the effects of aerosol and climate, will remain uncertain in models. This WP will implement the latest emission inventories and formation mechanisms in both global and regional aerosol microphysics models, along with detailed process models, evaluate them against observations, and determine how different particle sources shape the particle size distribution and number.

Work Package 2.5 started at the beginning of Month 18, in the second half of Year 2. The specific objectives of Work package 2.5 at the beginning of Month 18 were:

- to assess the relative contribution of primary and secondary particle emissions to total particle number in different size ranges and environments (Task 2.5.1);
- to assess the relative contribution of natural and anthropogenic particle emissions to total particle number in different size ranges and environments (Task 2.5.2);
- to evaluate long-term changes in particle concentrations in different environments (Task 2.5.3).

ONGOING AND FUTURE WORK

Task 2.5.1

First model runs on the global impact of secondary particle formation on CN and CCN numbers have been conducted with a global CTM GLOMAP (Spracklen et al., 2006, 2007). Recently, the CN numbers produced by GLOMAP were evaluated against a number of global field sites as in the earlier studies comparison was concentrated on stations in Finland and central Europe. Generally the agreement between the observations and the model runs is good, using a simple scheme based on linear or square dependence on sulphuric acid for boundary layer nucleation (introduced in WP 1.1, see also e.g. Kulmala et al., 2006; Sihto et al., 2006; Spracklen et al., 2006). The results suggest a clear influence of secondary particle formation on the total CN numbers, particularly on their seasonal behaviour. A regionally-nested version
of GLOMAP is under progress. This will allow for studying secondary aerosol formation in a smaller scale.

Regional 3D-model PMCAMx-UF has been developed (Jung et al., 2008; Jung 2008). The model simulates the aerosol number (from 1 nm to 10 μm) and mass distributions for a variety of chemical components. PMCAMx-UF has been tested for the Eastern part of the United States while waiting for the necessary emission inventories and e.g. meteorological field data from Europe. To test the impact of boundary layer nucleation on aerosol number, the model allows the user to user can select among 6 different nucleation parameterizations. In the conducted studies it was found that model runs using scaled ternary water – sulphuric acid – ammonia nucleation parameterisation (Napari et al., 2002), for instance, serve well in predicting the particle formation and growth events observed in Pittsburgh, USA.

In the upcoming 18 months more global and regional model experiments with GLOMAP and PMCAMx-UF will be carried out to quantify the relative contribution of particle formation and primary emissions to observed particle number concentrations in different size ranges and in different environments. GLOMAP will be run with regional nests over 3 environments (central Europe, northern Europe and Boreal regions, and a remote marine site such as over Cape Grim) and PMCAMx will focus on the European region. The latest particle formation schemes from WP 1.1 and 1.2 and new size-resolved primary particle emission inventories from WP 1.3 will be implemented in the models and the relative contributions of particle formation in boundary layer and nucleation in free troposphere to the total particle number will be studied. The models will be evaluated against existing observations from ground stations and against new observations made during the EUCAARI field phase and airborne measurements in 2008 (WPs 2.1, 2.2, 4.2, 4.3), and a model intercomparison will be undertaken to better understand the model processes that are important for a realistic simulation of nucleation events and growth to CCN sizes.

Task 2.5.2

Global model runs studying the effect of anthropogenic and biogenic emissions on particle formation have been conducted with GLOMAP (Spracklen et al., 2008). It was observed that boundary layer nucleation and emissions of biogenic organics are coupled, when looking at their effect on CCN numbers. It was observed that on average the forest emissions increase boreal CCN with about 100%. However, in a run without nucleation the forest emissions increase CCN by only 50%. Thus, forest terpene emissions are twice as effective at producing CCN if nucleation occurs.

The contribution of biogenic SOA formation on total aerosol mass has been estimated using a physicochemical box model applied in a Lagrangian manner over Scandinavia (Tunved et al., 2008). A recently-developed parameterization for the aerosol mass yield from biogenic terpenes was used (see also Tunved et al., 2006). It was concluded that the needle-leaved forest above 58°N alone is capable of producing aerosol mass concentrations corresponding to 12-50% of today’s total values in the boundary layer – giving the minimum estimate for the biogenic influence on particle mass. It was also demonstrated that the forest itself could produce up to 200 CCN per cubic centimetre on average over Scandinavia.

Generally, the developments of GLOMAP and PMCAMx-UF described above (in connection with Task 2.5.1) will allow for new model runs assessing the natural versus anthropogenic impact on total particle numbers.

Task 2.5.3

Preliminary model runs comparing global CCN, cloud droplet numbers (CDN) and cloud reflectivity in 1850 and 2000 have been conducted with GLOMAP. The results indicate that the global impact of nucleation on the 1850-to-2000 change in cloud reflectivity is small (few percent) but regionally it may be as high as 50% and can be either positive or negative. These early results suggest that boundary layer nucleation will be important in indirect forcing calculations on a regional scale.
In the future more model runs will be made to assess the long-term development of particle, CCN and cloud droplet numbers. These model runs will be compared to field observations, when available.

REFERENCES


INTRODUCTION

Anthropogenic aerosol particles such as sulphate and carbonaceous aerosols have substantially increased the global mean burden of aerosol particles from pre-industrial times to the present-day. One of the biggest unknowns is the role of aerosols acting as cloud condensation nuclei (CCN) and as ice nuclei (IN). The increase in cloud droplet number due to an increase in anthropogenic aerosols for a given cloud water content increases the cloud albedo. In addition, the precipitation efficiency of warm clouds is reduced, possibly increasing cloud lifetime (aerosol cloud lifetime effect). Both effects remain to be very uncertain (Denman et al., 2007). Here, laboratory studies are used to evaluate the ability of aerosols to act as CCN and IN. The CCN studies are complemented with Lagrangian parcel model simulations. First results from the Cabauw measurement campaign in May 2008 will be presented.

Task 3.1.1 Laboratory studies of the ability of aerosols to act as CCN:

Pandis et al. (FORTH) have investigated in a series of laboratory experiments the CCN activity of secondary organic aerosol and the change of its activity with time. Systems that have been investigated include SOA produced from the oxidation of a-pinene, b-pinene, limonene, carene, and b-caryophyllene as well as their mixtures. Simple parameterizations that can be used in global models have been developed describing the activation of these SOA particles. The SOA becomes more CCN active in all cases due to reactions with the OH radical (Figure 1). The results of this work are described in Engelhart et al. (2008) and Asa-Awuku et al. (2008).
**Figure 1.** Change of the activation diameter with time of b-caryophylene SOA in the presence of OH radicals for supersaturations 0.6% (grey squares) and 1.1% (green circles). Also shown (red circles) the activation diameter of aerosol passed through a thermodenuder at 40°C prior to exposure to 1.1% supersaturation.

Task 3.1.2 Laboratory studies of the ability of aerosols to act as IN:

The recently developed Zurich Ice Nucleation Chamber (ZINC) as described by Stetzer et al. (2008) was used to explore ice nucleation of size-selected mineral dust particles in the mode of deposition nucleation at temperatures from -20°C to -55°C. Four different mineral dust species have been tested: Montmorillonite, Kaolinite, Illite and Arizona Test Dust (ATD). The selected particle sizes are 100 nm, 200 nm, 400 nm and 800 nm. Relative humidities with respect to ice (RHi) required to activate 1% of the dust particles as ice nuclei (IN) are reported as a function of temperature. An explicit size dependency of the ice formation efficiency has been observed for all dust types (see for example, Figure 2). In addition, a possible parametrisation scheme for the measured activation spectra is proposed, which might be used in modeling studies. Results will be presented at the EUCAARI meeting.

**Figure 2:** RHi required for 1% activated fraction as a function of temperature of montmorillonite dust particles for different particle sizes. The water saturation line is shown as a solid, black line. The breakthrough line marks the region where water drops condensed in the nucleation section, grow large enough to pass the evaporation section (Welti et al., in prep).

Task 3.1.3 Analysis of airborne data: Plans for the next 18 months

20 scientific flights were carried out during the IOP IMPACT campaign around the Cabauw region in May 2008 for various meteorological conditions (cloudy and clear sky). Measurements included airborne characterization of thermodynamics and turbulence, radiation (radiances and fluxes), remote sensing (incloud reflectivity, attenuated backscatter, ...), cloud microphysics (droplet concentration, droplet size distribution, LWC, ...), and physical, chemical and optical properties of aerosol and CCN by using a combination of isokinetic aerosol inlet (CAI) and a CVI installed on the ATR-42 research aircraft of Météo France. Instruments onboard included CPC, OPC, SMPS, CCNC, AMS, PSAP, nephelometer, gas analyzer, radar and lidar. Analysis of these data is in progress by Laurent Gomes and Hanna Pawlowska. A relevant data base is under construction.

Task 3.1.4 Lagrangian parcel model simulations:
During the year 2008 were carried out field campaigns at the EUCAARI supersite Cabauw and at other two EUCAARI sites: San Pietro Capofiume (Italy) and Mace Head (Ireland). Therefore, the chemical analysis and the elaboration of simplified inorganic/organic chemical composition for aerosol sampled in these experiments are in progress.

The simplified inorganic/organic chemical composition for different aerosol types will contain inorganic species (sulfate, nitrate, sea-salt), insoluble species (dust, water insoluble organic carbon -WINC), water soluble organic carbon (WSOC) species (neutral compounds - NC, mono- and di-acids - MDA and polyacids – PA). Figure 3 shows such simplified chemical compositions of aerosol as a function of size for polluted and background aerosols sampled at San Pietro Capofiume during the EUCAARI campaign. The number of ions and moles is overestimate up to ca. 0.6% by considering only sulfate ((NH$_4$)$_2$SO$_4$), nitrate (NH$_4$NO$_3$) and sea-salt (NaCl) instead of all possible inorganic compounds such as NH$_4$Cl, MgCl$_2$, NaNO$_3$, Na$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, NaCl.

Representative molecules for the three classes of WSOC will be chosen for Lagrangian parcel modeling by Mircea (ISAC) based on the results from WP 2.1, WP 2.4 and WP 1.4.

An aerosol-cloud chemistry process model was used by O’Dowd and Flanagan to simulate the growth of aerosols in the marine environment. The model consists of a thermodynamic equilibrium module based on Pitzer thermodynamics Pitzer model method (see Pitzer 1991) and a mass and heat flux module (Hienola et al., 2001) was incorporated to simulate non-equilibrium growth. The model was used to simulate cloud droplet activation and sulphate production in marine stratiform clouds.

An externally mixed sea-salt sulphate aerosol population was studied and the effect of organic acids on activation and sulphate production investigated. The dry sea-salt aerosol population was represented by the sum of two lognormal curves, one of mode radius 0.1 μm, corresponding to film droplet production and the other of mode radius 1 μm corresponding to jet droplet production. The geometric standard deviations of the two modes were 1.9 and 2.0, respectively and the total concentration was 53.3 cm$^{-3}$. It
corresponds to high wind speed conditions over the ocean. The dry sulphate aerosol was represented by a single log-normal curve of mode radius 0.075 μm. The sulphate concentration of 44 cm⁻³ represents the mean concentration of sulphate aerosol particles for winter maritime air observed over the North Atlantic (O’Dowd et al., 2000).

The effect of nitric, acetic and formic acid on activation and in-cloud sulphate production was investigated. The addition of acids dramatically reduced the sulphate production. Just 0.1 ppb of HNO₃ reduces the amount of sulphate produced from 6.49 μg kg⁻¹ air to 4.1 μg kg⁻¹ air, a reduction of almost 37%. It was found that the reason for this reduction is that the presence of HNO₃ reduces the pH of the solution droplets, which inhibits the ozone-driven pathway of sulphate production. Acetic and Formic acid also caused a reduction in sulphate production but of lesser magnitude than HNO₃ as they do not cause as large a reduction in the pH. The effect of nitric acid on the activation was also studied and for the given simulation the addition of 0.1 ppb HNO₃ caused a 3.2% increase in the activated fraction.

Task 3.1.5 Radiative closure:

In the last months Horn and Kloth (IfT, Leipzig) validated the three-dimensional large eddy model simulation (LES) version of the model ASAM with the DYCOMS-II-Case of the GCSS-Cases, using a simple microphysical approach. Parallel to this they developed a particle based aerosol growth model to study the evolution of a given aerosol size distribution during the activation process and cloud-droplet formation.

The goals for the next 18 months are further validation of the LES-Model. Beside that, they will use the particle based growth model to develop a bulk microphysics scheme with 4 modes (unactivated aerosol, activated/growing aerosol, cloud droplets, rain), each a log-normal-distribution with 2 (perhaps 3) moments and implement this bulk-scheme into the LES-model ASAM.

After that the radiation model of Fu and Liou (1992), which is already implemented in the ASAM code will be added. This allows comparison of the radiation of single columns in the heterogeneous cloud field to the results with the mean state of the whole domain and the measurements during the IOP in Cabauw.

A two-core parameterization of the aerosol optical properties is being developed at CNRM by Gomes and Brenguier to be coupled with the radiation scheme of MesoNH. It will be used to study the absorption and diffusion of short wave by in-cloud and out-cloud aerosols and their impact on the cloud life cycle. The aerosol radiative impact will be also studied by using airborne measurements of physical and chemical aerosol properties. In addition, data collected the EUCAARI IOPs (thermodynamics and cloud microphysics) and simulations will be jointly used to study the stratocumulus-cumulus transition.

Overarching/open questions:

1) Is there a useful intercomparison of Lagrangian parcel modeling that should be done? Either starting from Jungfraujoch data (from Urs Baltensperger) or from Mihaela Mircea’s data?

2) Are there compounds which would make sense to be studied with different CCN counters and with different groups?

REFERENCES


Assessment and quantification of the aerosol indirect climatic effects: WP 3.2

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Keywords: Aerosols, clouds, radiation, measurement campaigns

INTRODUCTION

WP 3.2 will assess experimentally the impacts of aerosol changes on the dynamics of boundary layer clouds, which are the most susceptible to aerosol anthropogenic changes. The methodology combines the collection of data during a long-term observation period followed by an intensive observation period, their analysis to characterize all terms of the energy balance, cloud-resolving modeling, and the quantification of the different factors’ contributions to the cloud life cycle.

WP3.2 contributes to EUCAARI objective 1a. Indirect radiative effects due to aerosol particles are posing amongst the largest uncertainties in the assessment of anthropogenic climate change. The effects of aerosol particles on planetary albedo have been extensively studied, but there is still little evidence that such aerosol effects could significantly affect the cloud life cycle and the formation of precipitation. The modulation of cloud albedo by aerosol particles, (first indirect effect), has been investigated during international field campaigns. In particular, the interactions between cloud droplet concentration, cloud albedo and the formation of precipitation have been corroborated by in situ and remote sensing measurements. However, the possible impacts on the cloud dynamics, including precipitation rate and the cloud life cycle, have not yet been assessed experimentally. Satellite retrievals have shown correlations between aerosol optical thickness as a proxy for aerosol concentration and cloud macro (liquid water path) and microphysical (droplet effective radius) properties. They do not yet provide enough information on the aerosol to assess how aerosols interact with clouds.

ONGOING AND FUTURE WORK

WP 3.2 has started in January 2007, some activities have ended (Task 3.2.1), other activities are ongoing or will start in the next period.

Task 3.2.1 [Intensive Observation Period (IOP): preparation and operation]
This task is now complete. Preparations for this experiment at Cabauw, Netherlands, started early 2007, soon after the start of EUCAARI. Preparations included detailed planning for aircraft operations, Air Traffic Control, the interaction with the EUCAARI LONGREX team, and the updating of infrastructure to sample aerosols at 60m altitude. The IOP took place in May 2008. Participants included not only the EUCAARI – partners mentioned in the title, but also many more national and international research institutes. These participants installed and operated their aerosol and cloud equipment at the Cabauw laboratory.
Task 3.2.2 [Nine-month characterization of aerosol and clouds at CESAR]
This task is now underway. The starting date of the period was 1 May 2008 [the start of the IOP]. Formally, the ending date is 1 February 2009. However, at this stage we plan to extend the time period to 1 May 2009. Also, significant cloud data is available prior to 1 May. This task mostly involves the semi-continuous operation in situ and remote sensing instrumentation for clouds, aerosols and radiation, of the national Cabauw Experimental Site for Atmospheric Research (CESAR) consortium, augmented by TNO - FMI’s aerosol equipment.

Task 3.2.3 [LES: Data analysis and case study simulations]
This task is now underway. Roughly speaking the period of May 2008 can be separated into a clear-air (1 – 15 May) and a cloudy (15 -31 May) period. This means that research will broadly pertain to clear – air (aerosol direct effects) and cloudy (aerosol indirect effects) topics of interest. An inventory of quick looks and data sets is being constructed at KNMI with the aim to facilitate the assessment of data quality vis-à-vis the research requirements. This data inventory is nearing completion. A workshop was held at CNRM, Toulouse in October 2008 to survey the data sets from the IOP in its most up-to-date form and to assure that participants of the IOP could forge further working relationships. An inventory of research topics and potential papers was made amongst the participants. Topics include a) aerosol nucleation. b) CCN – CDNC closure c) Radiation closure and d) LES simulation studies. In the next period, research, which was listed in this inventory, will be initiated.

Task 3.2.4 [Assessment of the aerosol impact on the cloud life cycle]
LES simulations of the cloud diurnal cycle, with diverse thermodynamic conditions and diverse aerosol properties, will be analysed to distinguish between the contribution of the meteorology and the contribution of the aerosol alone. Their respective contributions to the terms of the energy balance will be quantified to assess the impact of aerosol on the cloud life cycle. The nine months observation period of ground and satellite measurements will be analysed to detect cases of similar features as the IOP case studies to extrapolate the results of the LES simulations. This task has not started, because not all data for the 9 month IOP has been taken.

Task 3.2.5 [Impact of aerosols, clouds on shortwave irradiance]
The first days of IMPACT were exceptionally cloudless and allowed us to perform a shortwave closure study, using readily available data. On the basis of AERONET products, the Doubling Adding KNMI (DAK) radiative transfer model, and BSRN measurements we obtained excellent closure. For around 70 cases we obtained differences between model and measurement of < 2 W/m2 for direct, diffuse, and global irradiance. In the next period a paper on this subject will be written and a similar analysis will be done on selected data of the cloudy period.
PARAMETERISATIONS FOR GLOBAL AND REGIONAL MODELS: WORK PACKAGE 3.3

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Keywords: Model, parameterization, global, regional, air quality, climate

INTRODUCTION

WP 3.3 aims to develop and test new parameterizations for global and regional scale models based on the results of detailed process studies and new mechanistic developments in other work packages. The approach here will be to evaluate the simpler climate model schemes against the full microphysical schemes and observations in a self-consistent way. This WP also tackles a major problem that limits the accuracy of indirect forcing calculations: modelling the sub-grid scale properties of the clouds and the structure of the boundary layer. No global models represent these meteorological processes realistically, so a major advance in the realism of global models can be made in this project. This WP brings together a state of the art range aerosol and cloud models on different scales to develop optimum parameterizations for the climate models. This approach means that the weaknesses of parameterizations can be determined against benchmark models and observations in a traceable way.

WP3.3 contributes to EUCAARI objectives 1 and 2. Global climate models and regional air quality models require highly simplified yet accurate schemes to describe the global and regional aerosol properties and the effect of aerosol on the climate. There are two principal challenges. Firstly, the complex chemical and physical properties of the aerosol (particle size distribution, chemical properties, mixing state, chemical transformation, etc.) must be represented efficiently, but any scheme must be capable of capturing the properties important for direct radiative forcing and changes in CCN. Secondly, model schemes are required to calculate the number of cloud drops as a function of aerosol properties and the microphysical evolution of cloud drop number in different clouds. In order to better represent boundary layer clouds, which are responsible for the majority of the indirect aerosol effect, the representation of the boundary layer needs to be improved such that the magnitude of the temperature and humidity inversions can be captured. Traditionally boundary layer clouds are underestimated in GCMs, which suggests that the indirect aerosol effect is underestimated.

ONGOING AND FUTURE WORK

WP 3.3 has started in June 2008, therefore the activities are ongoing.

Task 3.3.1
The University of Oslo have reformulated the treatment of detrainment of cloud water from shallow convection, to avoid excessive cloud droplet numbers over the subtropical oceans and modified the
formulation of cloud droplet nucleation by replacing the symmetrical pdf for vertical velocity (Ghan et al., 1997) by a constant vertical velocity formulation. Further testing and tuning will be conducted before a new frozen CAM-Oslo is obtained. Participation in AeroCom’s new inter-comparison for the aerosol indirect effect will provide the needed validation of the new formulations.

Task 3.3.2
Oslo has now started experimenting with alternative formulations of the subgrid scale vertical velocity, including non-symmetric pdf, a constant vertical velocity, and a different dependency of vertical velocity on turbulence. Results so far indicate that the cloud droplet number concentration is very sensitive to this formulation. A weakness with the symmetric pdf seems to be that even in areas of large-scale rising motions, a large fraction of the grid box will have a negative vertical velocity because of the left hand tail of the pdf.

They will investigate the sensitivity of aerosol indirect effect estimates to the formulation of cloud cover in the CAM-Oslo. Subsequently, they will compare the relationship between aerosol number and cloud properties using different formulations of cloud cover with satellite estimates.

Task 3.3.3
It has been observed that the stratocumulus are too shallow to be well represented in the standard vertical grid of ECHAM5. To better simulate these low clouds without increasing the vertical resolution tremendously, ETH-Z added two levels dynamically wherever a stratocumulus could form. The new interfaces are following the inversion at the cloud top and the lifting condensation level (LCL) at the bottom of the cloud. The algorithm, which computes the cloud top and the vertical thickness of the stratocumulus-topped boundary layer in ECHAM5, and defines the new grid has been implemented. The implementation of the interaction between this new grid and the cloud microphysics, radiation and the other physical processes in ECHAM5 is still work in progress.

Furthermore ETH-Z worked on implementing a simple bulk entrainment parametrisation in the cloud routine in ECHAM5. With the changes the cloud coverage in all the stratocumulus regions has been significantly improved.

Finally based on conserved variables diffusion, three different explicit entrainment parametrisations were chosen to be tested in ECHAM5. The effect of the low levels clouds on climate change will be studied.

UiO will introduce a non-symmetric pdf for vertical velocity, based on theoretical studies, for calculations of sub-grid scale cloud droplet activation in the CAM-Oslo.

Leeds aims to optimise the representation of the particle size distribution and microphysics using existing observations and case studies. This work will then be extended to include new observations.

Task 3.3.4
Leeds will use the Global Model of Aerosol Processes (GLOMAP) which runs with either a sectional or modal aerosol scheme to compare aerosol size distributions against observations in different atmospheric regions and identify weaknesses in the modal microphysics. SU will in cooperation with FMI and Leeds perform inter-comparison and sensitivity tests, including measured data, with a Lagrangian type box model based on the UHMA model and the GLOMAP model to evaluate the aerosol and cloud representation.

Task 3.3.5
TNO and JRC will examine the effect of model spatial resolution on microphysics and development of the size distribution. They will use a hierarchy of models, including the CTM-TM5 coupled to the M7 modal...
aerosol scheme (running from $6^\circ \times 4^\circ$ to $1^\circ \times 1^\circ$ resolution) and the mesoscale model LOTOS also coupled to M7 (running from $1^\circ \times 1^\circ$ to $0.25^\circ \times 0.125^\circ$ (10 km x 10 km)).

REFERENCES

INTRODUCTION

WP 3.4 aims at improving our ability to quantify the spatial distribution and variability of particulate air pollution over Europe in terms of particle number, mass concentration, composition and visibility. In this WP the new parameterizations of nucleation processes, the state of the art chemical mechanisms and the emissions will be incorporated in Regional and Global scale air quality models. These models will in turn be used to estimate how air pollutants and aerosol levels change with transport over urban cities and how aerosol levels affect gas phase chemistry. In addition, we will be able to quantify the feedback processes that link climate change and atmospheric aerosols.

Contributing aims to this general objective are:

- Improvement of the predictive ability (PM number, mass, size/composition distribution) of regional scale CTMs over Europe using the results of EUCAARI laboratory and field studies and the corresponding theoretical developments.
- Investigation of the pollution exchange between the major urban centers in Europe and the regional background (effects of the urban centers on continental pollution and regional contributions to local air pollution).
- Quantification of the effects of a changing climate on urban and regional air quality in Europe.
- Investigation of the effects of changing emissions for improvement of urban and regional air quality on aerosol radiative forcing over Europe.

ONGOING AND FUTURE WORK

WP 3.4 has started in Month 10 of the program, therefore the activities are ongoing.

Task 3.4.1

FORTH has improved the inorganic aerosol thermodynamics, the secondary organic aerosol formation and the primary organic aerosol dynamics modules used in the regional CTM PMCAMx. The ISORROPIA module has been replaced with the recently developed ISORROPIA-II. New primary and secondary organic aerosol modules have been developed using the Volatility Basis Set approach of Donahue et al. (2006). IFT has improved the modelling system COSMO-MUSCAT by the following features: Extension of the used modal aerosol model M7 by incorporating nitrate, ammonia and selected organics, improvement of the sea salt
emission module, computation of extinction coefficients from simulated aerosol distributions, development of a preprocessor for the generation of lateral boundary values from global CTM simulations (implemented for ECHAM5 data) and tools for the comparison between model simulations and measurements. UiO has improved the aerosol modelling capacity of the Oslo CTM2 by the addition of a secondary organic aerosol (SOA) scheme. A total of 18 organic precursor species are accounted for, which contribute to SOA formation, 13 of which are biogenic and 5 of which are anthropogenic in origin.

Task 3.4.2
UAEG, in collaboration with FORTH, has focused its effort in adopting PMCAMx for Europe. In addition wind fields for the specific periods of interest had to be produced for the extended European Domain, using WRF. For the emissions UAEG received and processed raw emission data as follows: Anthropogenic emissions: GEMS and Biogenic emissions: NATAir. UiO has used the Oslo CTM2 to examine the regional and global effect of anthropogenic emissions from China. The participants in this WP plan to focus on the application of their comprehensive CTM models over Europe. Specifically, they will study, how the concentrations of air pollutants and aerosol change with transport over urban centers, how aerosol levels and size distribution affect gas phase chemistry and how aerosol properties change with changing emissions over Europe. The nesting capabilities of the CTMs will be used to study the effects of local fluxes of primary pollutants for regional scale and vice versa.

Task 3.4.3
FORTH has examined future (2050s) ozone (O3) and fine particulate matter concentrations over Europe by performing and analyzing various global climate-chemistry-aerosol simulations. In the immediate future the WP participants will start studying the link between climate and the processes that affect the concentrations of primary and secondary aerosols.

REFERENCES

INTRODUCTION

WP 3.5 aims to improve our understanding of the role of aerosol particles in the climate system by developing and applying numerical climate models including parameterizations of aerosol and aerosol-cloud processes. Model simulations are carried out to assess the performance and sensitivity of current model versions and new model approaches, as well as the importance of specific processes and their contribution to radiative forcing.

Contributing aims to this general objective in the period 12-30 months are:
- Testing and evaluating new parameterizations
- Assessing the models’ sensitivity to model approaches
- Assess direct radiative forcing DRF and compare to observations
- Statistical analyses of extreme events – methods

ONGOING AND FUTURE WORK

The coarse resolution of global models in space and time requires the parameterizations of many aerosol processes. These parameterizations are not always well constrained, because observations on the relevant scales are lacking. A process particularly uncertain is the formation of new aerosol particles. As nucleation from the gas phase may significantly increase concentrations of tropospheric cloud condensation nuclei, the indirect aerosol effects are affected by uncertainties in the nucleation parameterization. In current implementations, formation of secondary particles is controlled by the availability of sulfuric acid gas, the surface area of existing particles, and the nucleation scheme.

We performed sensitivity simulations to investigate how sensitive the aerosol direct and indirect effect is against changes in the nucleation parameterization. Nucleation of sulfuric acid gas is the major mechanism initiating the formation of secondary particles. Figure 1 displays the effect of the formation of secondary sulphate particles. Secondary particle formation contributes to the number concentration and the aerosol optical depth. Moreover, we found that secondary particle formation impacts significantly the cloud condensation nuclei and cloud droplet concentrations.

But a comparison with EMEP surface measurements showed that the agreement between model calculated sulfur species concentrations and observations is far from being satisfying.
New schemes include in addition to sulfate SOA as secondary compound. However, it is assumed that SOA does not form new particle. The presence of condensable organic species influences the rate of growth of an aerosol population, allowing small particles to grow into the size range where they are optically active in the visible spectrum and where they may act as cloud condensation nuclei. Figure 2 displays the contribution of SOA to the aerosol fraction which serves as CCN. Addition of organics enhances the mass of CCN by 10 to 20%.

Figure 1. Difference in annual mean AOD in % between the standard and the no-nucleation experiment.
Figure 2. Ratio of SOA to total aerosol of the fraction of total mass of "potential CCN" (the fraction with aerosol radius > 35 nm) as calculated using ECHAM5-HAM.

Regarding the aerosol cycle the main uncertainties and model differences arise from:

- Dry deposition flux of sulfur dioxide
- Wet removal of sulfate particles
- Choice of the nucleation scheme

Moreover, we found an increasing deterioration of the agreement with observations in the period 1980 to 2000 for sulfur dioxide but not for sulfate mixing ratios which needs further investigations. Next steps are evaluation of nucleation rate and internal aerosol properties by comparison to field measurements. A short-term goal of WP 3.5 is to provide an evaluated aerosol-cloud modul for use in models applied for the next IPCC assessment until mid 2009.

To compare with model calculations a new aerosol climatology based on quality data from ground-based remote sensing networks merged into multi-model median background fields was developed by Stefan Kinne. This data have been used to derive radiative forcing of aerosol for clear sky and cloudy conditions (Figure3). Particularly interesting, the radiative forcing at TOA is significantly reduced by the presence of clouds.
Figure 3. Aerosol radiative forcing for clear sky (upper two rows) and for cloudy sky (lower two rows) at top of the atmosphere (1st and 3rd row) and at surface (2nd and 4th row). Solar and infrared (left graph), solar (mid graph), and anthropogenic part (left graph).
FEEDBACK PROCESSES AND INTERACTIONS: WORK PACKAGE 3.6

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Keywords: aerosol, climate feedbacks, radiative effects, Earth system modelling

INTRODUCTION

WP 3.6 aims at understanding interactions and feedbacks in the Earth System, which involve aerosol processes and properties. The workpackage will assess the strength of climate feedbacks involving aerosol precursors and aerosol species. It relies on other EUCAARI WPs to improve parametrisations used in Earth System models. The workpackage focuses on the simulation setup for the next IPCC assessment report.

ONGOING AND FUTURE WORK

WP 3.6 has only started in July 2008, therefore the activities are ongoing.

A paper is being drafted that reviews current knowledge on the role of aerosols in climate feedbacks. Each one of the various feedback loops involving natural and anthropogenic aerosols that have been identified in the past are assessed from the existing literature. Research directions are also discussed.

Activity in WP3.6 has focused on preparing climate models ready for the IPCC AR5 simulations that are due in 2010 and will constitute the backbone of WP3.6. The HadGEM2-ES will include interactive aerosols, coupled to the tropospheric chemistry scheme through interactive oxidants, and coupled to the marine carbon cycle through emissions of DMS and deposition of dust. A 100-year test simulation has been undertaken to assess the coupling between atmospheric chemistry and aerosols. The ECHAM model will rely on the M7 scheme and will also include a parametrisation for BVOC emissions. A scheme for secondary organic aerosols is being implemented in the IPSL-INCA and ECHAM models. Equilibrium runs of 100 year duration for pre-industrial and present day aerosol sources were done with the new fully coupled IPSL-INCA model and showed a stable response of the climate system to an interactive aerosol component perturbation. This model development task is expected to be completed by July 2009 and IPCC simulations will start soon after. The Earth System models will be used to investigate the climate feedbacks involving DMS and sulphate production, biomass burning, dust and SOA.

A transient climate simulation was performed with the ECHAM model to study the response to global warming of dimethylsulfide (DMS) in the ocean, the DMS flux to the atmosphere, and the resulting DMS concentrations in the atmosphere. The DMS production and consumption processes in the ocean are linked to plankton dynamics simulated in the marine biogeochemistry model HAMOCC5.1, embedded in an ocean general circulation model (MPI-OM). The atmospheric model ECHAM5 was extended by the microphysical aerosol model HAM, treating the sulfur chemistry in the atmosphere and the evolution of microphysically interacting internally and externally mixed aerosol populations. For future conditions (2000–2100) we assume greenhouse gas concentrations, aerosol and aerosol precursor emissions according to the SRES A1B scenario. We analyzed the results in terms of simulated changes between the period 1861–1890 and 2061–2090. For the global annual mean DMS sea surface concentration and the DMS flux we found a reduction by 10%. The DMS burden in the atmosphere is reduced by only 3%,
owing to a longer lifetime of DMS in the atmosphere in a warmer climate (+7%). Regionally the response and the underlying mechanisms are quite inhomogeneous. The largest reduction in the DMS sea surface concentration is simulated in the Southern Ocean (~40%) caused by an increase in the summer mixed layer depth, leading to less favorable light conditions for phytoplankton growth. In the mid and low latitudes DMS sea surface concentrations are predominantly reduced due to nutrient limitation of the phytoplankton growth through higher ocean stratification and less transport of nutrients into the surface layers.

REFERENCES


FIGURES

HadGEM2-ES aerosol feedbacks

Figure: Schematic of the aerosol processes and feedbacks included (in green) or not included (in red) in the HadGEM2-ES model.
GROUND SITE DEVELOPMENT AND AEROSOL CHARACTERIZATION IN DEVELOPING COUNTRIES

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Keywords: aerosol, measurement, knowledge transfer, developing country

INTRODUCTION

Studies that have investigated number size distributions or concentrations of aerosol particles in Asia, Latin America or Africa are very few (e.g. Baumgardner et al., 2000; Jayaratne and Verma, 2001; Mitra and Sharma, 2002; Mönkkönen et al., 2004a; Mönkkönen et al., 2004b; Wehner et al., 2008; Wu et al., 2008; Laakso et al., 2008) even though the air pollution problem is particularly serious in the mega cities of South and East Asia. Especially, cities like Delhi, Kolkata (Calcutta), Mumbai (Bombay), Dhaka, Karachi, Bangkok, Beijing, Shanghai, Jakarta, and Manila are concerned to be one of the most polluted cities (Balsano et al., 2003, Faiz and Sturm, 2000). The major source of particulate matter (PM) and air pollution in the above mentioned megacities is due to rapid urbanization and increasing energy production, vehicle density, and industrialisation (Faiz and Sturm, 2000). The emissions from internal combustion engines have been regulated solely on the basis of total PM emission even though ambient particulate matter can also be characterized by other parameters like number concentration, mass size distribution, number size distribution and modality of size distribution.

Due to their rapid development, China, India, South-Africa, and Brazil are main contributors to air pollution in the corresponding regions. China and India will become more and more significant players in the global economy with all the accompanying problems of water, soil, and air pollution. Large regions in these countries are strongly influenced by particulate emissions, a fact visible due to satellite observations. Brazil is a main contributor to the haze over South- America mainly due to biomass burning. South Africa is one of the main producers of electric power in the southern part of Africa and contributes significantly hereby to regional aerosol formation. The atmospheric aerosol and its regional and global impacts are much less investigated and understood in such rapidly economically developing countries than in Europe or North America. Furthermore, regional air quality is rapidly changing and short-term measurements cannot reflect the actual situation. Good quality long-term data sets of physical, chemical, and optical characteristics are rare, and these are urgently needed to underpin policy making. Intensive field studies by the international community brought some insights, but not enough to understand quantitatively the impact on regional climate and air quality.

METHODS

Four measurement stations were established outside Europe in beginning of 2008. Their location was chosen to represent major regional pollution sources in four different countries in three continents. In Asia measurement sites are close to two mega cities, Peking and New Delhi. In South-Africa the site is in a heavily industrialized area and in South-America the site was chosen so that particulate matter from forest fires and continental Amazonian background can be monitored. To reach the goal of representative measurements, a sampling site for regionally aerosol measurements were be established in cooperation
with selected local partners. To obtain a useful data set for climate and air quality issues, in-situ aerosol parameters measured on ground should be combined with vertical aerosol information. The in-situ parameters measured are the light scattering coefficient (nephelometer), light absorption coefficient (absorption photometer) and number size distribution (mobility size spectrometer). Chemical characterization of particles will be by filter sampling with size ranges, P10 and PM1. For the vertical aerosol information Raman lidars will be used along with sun photometers. A Raman lidar provides the vertical profile of the extinction coefficient and additionally information about the boundary evolution and possible aerosol layers in different altitudes. The total measurement period for the in-situ measurements is planned to be two year, while for the filter sampling and lidar measurements only a period of one year is foreseen.

As an example of the results, we show here new particle formation, which was observed at all the sites events but with different frequency. In Figure 1, data from Elandsfontein in South-Africa are shown. Events of new particle are observed every day during the example period. Number concentration before events were typically several thousands particles cm$^{-3}$ while during the events the concentration increased up to approximately 50 000 cm$^{-3}$.

![Figure 1: New particle formation events in Elandsfontein, South-Africa](image)

In Manaus, Brazil, new particle events were not observed frequently (rainy season). The background concentration is typically very low compared to other 3 sites, order of few hundreds of particles cm$^{-3}$. During the event, the number concentration increased approximately by a factor of three.

In Gual Pahari, India, events are also observed everyday during the period presented here. The background number concentration is highest of the cases here, order of 10 000-20 000 cm$^{-3}$. During the events, the number concentrations increased up to a factor of four.
Figure 2: New particle formation event in Manaus, Brazil.

Figure 3: New particle formation events in Gual Pahari, India. Note that the grayscale is inverse than in figures 1 and 2.
Shangdianzi is a station on the border between clean (northerly winds) and polluted air masses from south, which can be seen by the abrupt changes in the contour plot of Figure 4. However, in spring and early summer, new particle formation was observed very frequently reaching number concentration of 50,000 cm$^{-3}$.

New particle formation events in boundary layer are observed in each site. The formation and subsequent growth of new aerosol particles in China, India, and South-Africa lead to a strong increase in CCN number concentration (Wiedensohler et al., 2008). In a quite clean site in Manaus, the contribution of a single event on the CCN and cloud formation might be different.

REFERENCES


Selection of super sites for Lagrangian studies using special instrumentation and specific questions posed by scientific WPs

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This work was performed under WP 4.2.1. This WP aims to provide a selection of sites that will be used by other WP’s to study transport and transformation between favorable sites located in the European measurement network. The work presented provides basis for selection of stations to be studied in detail during intensive observation periods (IOP’s) and also indicate where to study transport in the free troposphere (FT) and allow for studies of the exchange between mixing layer and FT (WP 4.3) as well as a selection of stations were advanced studies will be performed. The selection of stations to be included in this study aimed to answer a number of key-question relation to aerosol transformation and deposition processes during selected types of air-mass transport. The main objective was to identify stations that are ¹ frequently inter-connected by air-mass transport, ² can accommodate and partly already do facilitate the necessary instrumentation to answer the scientific questions posed and ³ help to answer the main scientific questions, mainly concerning transformation processes in different types of air-masses. The main scientific motivation for the selection was to find transport conditions that allowed to study:

- Ageing of ”Boreal” air masses as transport over continental sources occur
- Ageing of ”Atlantic” air masses as transport occurs over continental sources
- Evolution of the continental aerosol over Europe in Easterly and Westerly transects
- Other advanced studies of aerosols at favorable locations/environments

For the boreal case, the selection of the stations was performed to improve the understanding on how the boreal aerosol evolve as it is transported southerly over continental sources: how fast is the ”natural” Scandinavia aerosol transformed to anthropogenic type aerosols, how fast/slow is continental aerosol signal diminished over forested areas? This in turn will help to evaluate effects on CCN properties, removal rates etc. The selection will help to address the role of biogenic aerosol in the mixed anthropogenic-natural aerosol system. The stations selected for the boreal case was Hyytiälä, Vavihill, Melpitz and Jungfraujoch. The transport in-between these selected stations are frequent on an annual basis, the stations has well established infrastructure and connect the relatively clean boreal region with polluted parts of continental Europe.
The selection of stations to represent the ageing of marine, Atlantic, air as it is transported over continental areas was performed in an equal fashion, in order to provide the measurement capability/efforts necessary to investigate e.g. how rapidly the marine signal is lost in boundary layer and FT, and to study transformation processes, vertical mixing and cloud interactions during the marine to continental transition. The stations included were Maze Head, Cabauw and Melpitz.

For the continental transport cases, mainly studying transport over continental Europe, we recommended the stations Melpitz, K-Puzta (and possibly also Kosetice).

Figure 1: The stations included in the study as well as typical transport times across the different transects

Concerning the advanced studies the Finokalia will facilitate measurements with AMS, Ion Spectrometer and possibly also TDMA measurements. SPC and JRC will provide measurements with HTDMA. This will mean that advanced studies also will be available for the Mediterranean environment.

The free troposphere will be represented by Jungfraujoch (JFJ) and Puy de Dome (PDD). PDD will host measurements with TDMA, Ion Spectrometer and LIDAR observations while JFJ will provide measurements with Ion Spectrometer, TDMA and AMS.
WORK PACKAGE 4.3: AIRBORNE INFRASTRUCTURE – LONGREX AND IMPACT INTENSIVE OBSERVATIONAL PERIODS

WP 4.3, LONGREX and IMPACT teams
WP Partners: CNRM, CNRS, DLR, IFT, SU (lead partner), UNIMAN
WP leader: Radovan Krejci (SU), radek@itm.su.se

Keywords: aerosol, airborne observations, boundary layer, free troposphere

INTRODUCTION

WP 4.3 aims at providing the EUCAARI consortium with the necessary facilities for airborne measurements in a form of state-of-the-art equipped research airplanes. The contribution of this work package also includes airborne campaigns planning, realization of field measurements and basic data analysis. Three instrumented aircrafts (BAe-146 FAAM, ATR-42 SAFIRE and DLR Falcon 20) with complementary instrumentation and performance formed a core of the operations for the scientific flights in EUCAARI. In addition instrumented helicopter from IfT, Leipzig, French Falcon 20 and British NERC Dornier 228 participated on EUCAARI airborne campaign supported solely by national funding. In terms of experimental infrastructures, instrumented aircraft constitute the link between local scale point measurements at ground sites and continuous satellite global observations. The airborne IOP took place in May 2008 and it was divided into two concurrent campaigns: EUCAARI LONG-Range Experiment (LONGREX) based at DLR, Oberpfaffenhofen, Germany and IMPACT campaign centred at Cabauw supersite in the Netherlands.

Five tasks form basis to pursue work in WP 4.3:

Task 4.3.1: Definition of the sampling methodologies, scientific payload and preliminary flight plans.
Task 4.3.2: Preparation of the airborne campaigns.
Task 4.3.3: Aerosol properties evolution along the West-East and North-South transects including semi-Lagrangian flights.
Task 4.3.4: Closure experiment on the aerosol activation process
Task 4.3.5: Eulerian experiment at the CESAR supersite

ONGOING AND FUTURE WORK

During 2008 tasks 4.3.2 – 4.3.5 were successfully completed and activities within WP 4.3 will be completed in early 2009.

Task 4.3.2: Preparation of the airborne campaigns.

In close coordination between DLR, FAAM and principal scientists the coordinated flight strategy for both aircraft was defined. The FAAM BAe-146 was given the task of characterizing mainly aerosol properties in the boundary layer and therefore flying in general on low level routes, whereas the DLR Falcon had the task of mapping the vertical aerosol distribution by lidar along the BAe-146 flight path, which requires flying on upper airways. In addition, the DLR Falcon planned vertical profiling of the entire tropospheric column with in-situ measurements in
regions of particular interest (e.g. close to ground observations sites operated during the EUCAARI IOP). The particular challenge was to realize these ideas over a very large region in Europe given constraints in aircraft operation and air traffic control (ATC). Flight permissions and support of science missions was applied for individually at the ATC organizations of 18 different European countries. As a consequence of these preparations the national ATC centers proved to be overall very supportive and flexible in handling the science flights during the campaign. Exception was French airspace, where strict regulations prevented from performing any measurements there. Operation of the HRSL (high spectral resolution) mode of the DLR lidar system using a very powerful nadir looking laser was also subject to special arrangement with national ATC centers and fortunately proved to be possible in a number of important measurement cases.

Preparations of the DLR Falcon deployment included substantial support of DLR for integration and certification of a customized airborne version of the New Air Ion Spectrometer (NAIS) build by the University of Tartu, Estonia.

The FAAM BAe-146 participation on EUCAAROI IOP profited largely also from synergy with nationally funded ADIENT project.

Summary of airborne IOP:

**Task 4.3.3:** Aerosol properties evolution along the West-East and North-South transects including semi-Lagrangian flights.

**Task 4.3.4:** Closure experiment on the aerosol activation process

**Task 4.3.5:** Eulerian experiment at the CESAR supersite

The meteorological situation during the first half of the campaign (flights up to May 14) was characterized by a rather persistent anti-cyclonic system located over central Europe. This situation favoured the build-up of pollution in the boundary layer over central Europe, which is the result blocking of long-range transport into central Europe and the absence of precipitation, which would cause wet removal of aerosol. In this situation a number of flights could be performed, with two particularly notable cases on May 8 and May 14, where high aerosol concentrations and very high aerosol extinction values were observed and both aircraft took measurements close to each other. These cases are expected to be particular well suited for closure studies (addressing aerosol optical properties, or radiation) and satellite product validation.

**LONGREX (6 – 23 May 2008)**

The EUCAARI-LONGREX campaign was performed during 3 weeks in May 2008 from Oberpfaffenhofen airport, the DLR Falcon’s home base in southern Germany. The FAAM BAe-146 aircraft was based in Oberpfaffenhofen between May 5 and May 22, 2008. The French ATR-42 SAFIRE came to Oberpfaffenhofen on May 9, 2008, for intercomparison measurements with the two other aircrafts. The French Falcon 20 used Oberpfaffenhofen for refuelling on one mission flight on May 21, 2008.

DLR hosted and maintained the project web page for the EUCAARI-LONGREX campaign (http://www.pa.op.dlr.de/aerosol/eucaari2008/) as well as a ftp server for temporary campaign data storage. Weather forecasts based on ECMWF data for flight planning were also prepared by DLR and are stored at LONGREX website.

The DLR Falcon performed altogether 16 flights in the EUCAARI-LONGREX instrument configuration during May 2008. Of these, the first flight on May 2 was an instrument test flight,
the last flight on May 24 was made for a project outside of EUCAARI. For EUCAARI altogether 48.5 flight hours were flown.

The FAAM BAe-146 aircraft conducted in total 15 flights during the detachment. In order to facilitate flight planning, the aircraft followed pre-determined low level routes across European air space.

The coordination between DLR Falcon and BAe-146 in general worked out very well. That both aircraft are flying close together at the same time, the Falcon high and the BAe-146 low, is very difficult to achieve operationally. That is because the two aircraft fly with very different ground speed in this configuration and also because they are in this case usually controlled by different ATC units. To illustrate where the coordination was particularly successful, Figure 1 depicts the DLR Falcon flight sections at high altitude (with lidar measurements), for all cases when the BAe-146 was flying at the same time and was closer than 100 km distance.

![Figure 1. Map of flight tracks of FAAM BAe-146 (pink) and DLR Falcon (grey) during the EUCAARI-LONGREX campaign in May 2008. Highlighted are flight sections where the lidar measurements of the Falcon where in very close coordination with the BAe-146 flying in the lower troposphere at the same time.](image)

**IMPACT**

In May 2008 the EUCAARI-IMPACT campaign was held at and around the CESAR site at Cabauw, the Netherlands. The IMPACT campaign consisted of two major components, ground based and airborne. Cabauw was a focal point also for the LONGREX campaign. Especially the period between May 5th and 12th when exceptionally clear sky days with relatively high aerosol loading and wind from the East. These data should complement the efforts of the LONGREX teams very nicely.
The aircraft involved with the IMPACT campaign were: SAFIRE-ATR42 stationed at Zestienhoven (Rotterdam airport in the Netherlands, IFT-ACTOS (helicopter) stationed next to the Cabauw site, NERC-Do226 stationed at Oxford. In addition, number of flights focused on turbulence measurements was performed by the Wageningen University SkyARROW within the Dutch boarders.

The ATR42 was the main aircraft with respect to the IMPACT campaign, responsible for observations of the optical, physical, chemical and hygroscopic properties of aerosols, cloud microphysics and aerosol and cloud radiative properties. It flew 20 scientific flights during the entire month of May with around 60 hours of total flight time. The helicopter team with the ACTOS remained within several nautical miles from Cabauw supersite and carried out aerosol, cloud and radiation measurements during 12 scientific flights. The ATC limitations and weather conditions resulted in only one true cloud flight for ACTOS, where the probe could enter the cloud while flying above well developed Cu. The other flights were all classified as aerosol flights. Due to its capability to stay close to the Cabauw tower the measurements should ideally fit in between the single point measurements made at Cabauw and the flight tracks by the ATR42, especially when the latter flew within Box A close to Cabauw (Figures 2).

The NERC Dornier performed five flights focused solely on high resolution radiation measurements including polarization. The data is intended for radiation closure studies, both for clear sky cases (May 11th) and (scattered) cloud cases (other flights). All details on the IMPACT campaign, the payloads of each of the aircrafts, quick looks and data can be found at the IMPACT website (http://www.knmi.nl/eucaari).

Figures 2: Predefined flight track and operational areas for airborne activities during IMPACT campaign

Figure 1: Boxes A and B as referred to in the table.

Figure 2: Flight pattern C

Figure 2: Flight pattern D
PRELIMINARY RESULTS AND DATA ANALYSIS

Basic processing and quality check of measured data started after the field campaign and are in progress. First results of data analysis were presented in a number of contributions to the EUCAARI IOP workshop in Toulouse, October 6-8, 2008. Majority of data sets will be submitted to the EUCAARI data archive during 2008 or in early 2009. Nevertheless, it is essential that data users inside the EUCAARI community make contact with instrument PIs to assure that data are used in meaningful way.

We have developed a series of analysis themes that will be the focus of our efforts over the next year. Some of these will be carried out in close collaboration with science teams from the other aircrafts and the ground sites as well as with modellers.

*Evolution of aerosol properties in European context*
Very good case studies obtained, e.g. successful closure experiment over the Atlantic in highly polluted, aged European air mass aiming at accurate determination of radiative effects of (anthropogenic) European pollution aerosol

*Nitrate observations and their relationship to optical properties*
Fine mode aerosol mass loadings observed by the AMS featured an increasing trend going from eastern to western Europe (Figure 3). Initial analyses also show that the increasing mass was generally associated with an increase in fine mode aerosol nitrate mass fraction (relative to non-refractory aerosol mass). This analysis theme will focus on describing these observations and investigating their implications on aerosol radiative forcing.

![Figure 3: Aerosol mass spectrometer mass loadings and nitrate mass fractions observed on low-level (< 2000 m) straight and level runs during EUCAARI-LONGREX.](Image)

*Positive matrix factorization of organic aerosol*
We have begun examining organic aerosol source types during individual flights through a positive matrix factorization (PMF) method. PMF is a statistical approach to identifying robust features within large data sets. When applied to AMS mass spectra, these robust features correspond to mass spectra representing specific organic aerosol types. The relative contribution

68
of primary to secondary organic aerosol may be distinguished. Furthermore, different types of secondary organic aerosol may be distinguished, which correspond to organic aerosol that has been oxidized to varying degrees in the atmosphere.

Characterization of black carbon concentrations and mixing state over Europe
We will analyze the SP-2 black carbon (BC) mass concentration data collected over northern Europe to examine its distribution and mixing state relative to air mass age and emission sources. The radiative impacts of black carbon depend strongly on its mixing state, so this information is crucial to accurate predictions of radiative forcing by aerosols. Our approach for this research theme will be similar to that described above for the nitrate analysis. The SP-2 BC data will also be used by other researchers to examine its relationship to the observed optical properties.

High pressure system case study
Flights B362-B374 characterized a strong high-pressure centered over northwestern Europe, providing a unique opportunity to study the evolution of freshly-emitted and aged aerosol over several days. This research theme will consist of a cross-platform approach to examine aerosol aging processing and their impacts on aerosol size, optical properties and composition.

CCN statistics, profiles and possible processing and aging effects
This research theme involves a statistical analysis of the cloud condensation nuclei (CCN) activity during the EUCAARI-LONGREX flights, and possible links between CCN activity and other measures of aerosol hygroscopicity.

Comparison of aircraft and AERONET observations
We will examine the relationship between aerosol observations made aboard the BAe 146 with ground-level data including aerosol optical depth observations made by several AERONET (Aerosol Robotic Network) sun photometer sites. This information will help us link the in situ observations with atmospheric column integrated observations.

Comparison of aircraft observations from the inter-comparison flight
This research theme involves a comparison of observations from the various aircraft platforms featured in EUCAARI-LONGREX. This will provide information about the reliability of the aerosol and gas-phase measurements made on each of the platforms. It will also aid the comparison of data from the various aircraft when they were not in close proximity, which may be done to examine aerosol aging and transport processes.

SUMMARY
- successful mapping and detailed observation of (pollution) aerosol distribution over Europe on large scale with two, partly three aircraft in May 2008
- unique measurement concept (which was complex to arrange with ATC) involving one high, one low flying aircraft to provide synergy of concurrent lidar & in situ measurements (essential for closure studies and validation of satellite retrievals)
- some very good case studies obtained, e.g. successful closure experiment over the Atlantic in highly polluted, aged European air mass aiming at accurate determination of radiative effects of (anthropogenic) European pollution aerosol
- several successful cases of almost concurrent vertical sounding by lidar (HSRL) and in-situ vertical profiling of aerosol physico-chemical properties
- data analysis will provide new data on physico-chemical and radiative properties of European pollution aerosol & transformation processes.
AEROSOL IMPACTS ON CLIMATE AND AIR QUALITY: INTEGRATION WITH
POLICY, WORK PACKAGE 5.1

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Keywords: Model, parameterization, global, regional, air quality, climate

INTRODUCTION
The objective in WP5.1 is to integrate the new results coming out of WP1.1-WP3.6 in EUCAARI to
address the science questions in EUCAARI in the policy framework of change in climate, air quality and
ecosystems. In WP5.1 the focus is on future changes. Historical data will mainly be used for validation of
models and to assess the understanding of the relationships between changes in earth-atmosphere fluxes of
trace species, and changes in climate, air quality and ecosystem impact. Policy oriented models for climate
change and ecosystem/air quality impacts are applied on scenarios of emission changes corresponding to
likely developments in economic sectors of society. Emission changes are here thought of in broad terms;
not only direct anthropogenic emissions but changes in the exchange of chemical trace species between
terrestrial ecosystems and the atmosphere which is a consequence of planned or inadvertent land use
changes.

ONGOING AND FUTURE WORK
Task 5.1.1 is to adapt the policy oriented models to the findings in the EUCAARI Emissions and
formation Element, the Transport and Transformation Element and the Climate and Air Quality Effects
Element. The aim is to improve the parameterizations of the continuity equation terms describing
emissions, transformations, transport and removal of aerosols in the models in WP 5.1. met.no works with
the update of SOA routines in the EMEP Unified model, the update of dry deposition routines and the
evaluation of BVOC and climate effects on O3 and PM levels in past and future scenarios. A review paper
on the formation, properties and impact of SOA is prepared and submitted to ACPD. met.no coordinated
the SOA modelling chapter of the review article (Hallquist et al., 27 authors). Another review paper on
Aerosol: Current and Emerging Issues is planned for submission to ACPD during October 2008. As well
as surveying the current state-of-knowledge concerning SOA, this review assesses the major challenges
ahead in laboratory, field and modelling studies of SOA. met.no has also contributed a summary of recent
knowledge of biogenic versus anthropogenic aerosol to a more general review, `Atmospheric composition
change: Air quality and health -a review’ by P. Monks et al. This review, organised through ACCENT but
with many EUCAARI partners, surveys emissions, atmospheric processing, aerosols, transport processes,
and impacts of air pollution. For BVOC emissions, there are a number of possible databases and
methodologies available for their calculation on the global scale, including MEGAN and others listed by
e.g. Arneth et al. (ACP, 8, 4605-). Several databases for land use and associated parameters (e.g. leaf-area)
are also available (some were reviewed in EMEP report 1/2008 (Tarrason and Gusev, eds.) These
databases are still being explored, but a new global BVOC emission implementation in the EMEP model
by early 2009 is anticipated.

Task 5.1.2 Aerosols, ecosystem impact, air quality and climate: The task is to calculate how potential
changes of emissions up to 2030 would influence health and ecosystem impacts of particles on a scale
covering Europe and beyond, and to calculate the resulting impacts of emission changes as well as climate
change, separately and together, on air quality and ecosystems. Scenario runs and analysis with the EMEP
model will begin after month 24 when the scenarios for 2030 are expected to be ready (IIASA). In 2008,
IIASA has developed global emission projections of air pollutants and greenhouse gases for the other
world regions up to 2030 by its European and Asian implementation of the GAINS model. These
projections employ national projections of the development of economic activity for all countries that are
included in Annex 1 of the Kyoto Protocol, and address the development of the remaining parts of the world in a more aggregated manner based on global scenarios developed for the IPCC. This allows a more comprehensive assessment of air quality impacts and the implications on radiative forcing to be carried out by the other project partners. IIASA is exploring the implications of greenhouse gas mitigation scenarios (i.e., of modified energy consumption patterns that release less greenhouse gases) on the emissions of air pollutants, and explores - with the other partners - the net impacts on radiative forcing.

Based on available archived TM5 runs, JRC has developed and applied methodologies and datasets for the evaluation of the global impact of surface $O_3$ on agricultural crops yields, surface $O_3$ on human health, PM on human health and nitrogen deposition on ecosystem. The impact assessment requires overlaying various types of datasets with the TM5 air pollutant gridded output. An important part of the work was dedicated to the collection and gridding of ancillary data on a global 1°x1° resolution. These datasets are now readily available to be directly applied for global impact assessment. More in particular, following global gridded maps were prepared, by processing published data in literature and available datasets:

Ozone and crops:
- Start of the crop growing season(s) for wheat, rice, maize and soybean (major sources: UN-ECE mapping manual, US Department of Agriculture, International Rice Research Institute)
- Flagging of the crop production areas for each separate crop (major sources: IIASA Global Agro-Ecological Zones report, FAO)
- Fraction of national production of the crop within each grid cell belonging to a country or region (major sources: IIASA Global Agro-Ecological Zones report, FAO, USDA)

Air pollutants and health:
- Enhancement factor for urban PM within urban grid cells (major source: EDGAR emission database, CIESIN gridded world population data set, in-house developed parameterisation for urban increment)

Nitrogen deposition: Flagging of natural ecosystems.

The methodology for the PM urban increment was further refined and validated, making use of available data from literature and monitoring programmes. A study on the global impact of ozone on crop yields has been published (Van Dingenen et al., 2009). (R. Van Dingenen, F.J. Dentener, F. Raes, M.C. Krol, L. Emberson, J. Cofala. (2009). The global impact of ozone on agricultural crop yields under current and future air quality legislation. Atm. Env., in press.)

Task 5.1.3 Aerosols and climate change: Radiative forcing and climate response of specific economic sectors. JRC has carried out an analysis of a nudged climate simulation with ECHAM5.5-HAMMOZ aerosol-chemistry-climate coupled model for the period 1980-2005, focused on the relationships between European emissions and near surface ozone and particulate matter concentrations, and comparison with air quality measurements in different world regions to test the model performance, in view of the model application in the task.

Max Planck Institute for Meteorology in Hamburg has finished a simulation using the atmosphere-chemistry-aerosol >> model ECHAM5-HAMMOZ (=ECHAM5&MOZART2&HAM)covering the period 1980 to 2005. That means, we provide a reanalyses of the gaseous and particulate chemical compounds of the atmosphere. The chemistry and the aerosol schemes are coupled in a way that the presence of aerosol particles impacts the photolyses rates and aerosols provide surface for heterogeneous reactions. A model description and some evaluation studies are published in Pozzoli et al., 2008, J. Geophys. Res., 113, D07308, doi:10.1029/2007JD009007, and Pozzoli et al., 2008, J. Geophys. Res., 113, D07309, doi:10.1029/2007JD009008. The model version had horizontal resolution T42 and 31 levels in the vertical and applied nudging using the ECMWF reanalyses and analyses data. A modified version of the RETRO emission inventory was used. The 25 year hindcast over Europe will be analysed for the relationship between European emissions and near surface ozone and PM2.5/PM1.0, and then composites of years with dry vs. wet summers resp. hot vs. cold, positive NAO vs. negative NAO etc. will be formed and analysed with respect to air quality.

Task 5.1.4 Cost-effectiveness analysis of aerosol mitigation strategies with different spatial scales.
EUCAARI PLATFORM - DATA: WORK PACKAGE 5.2

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Keywords: database, model output, data, aircraft, measurements, global, regional, air quality, climate

INTRODUCTION

WP 5.2 has the primary objective to create a web-accessible database of measurement data and model output with a focus of providing aerosol model validation tools. The EUCAARI database integrates on a single platform all data collected within the project as well as relevant data from other sources. Data will be made accessible to the project partners in a common format via a convenient internet-based interface that also allows searching for data and producing of simple plots (e.g., of time series, or of the data geolocation). A Lagrangian dispersion model will be run 20 days backward in time from all measurement platforms collecting in situ data during EUCAARI for source-region identification. Results will be linked directly to the measurement data. Product Assurance and Quality Assurance (PA/QA) tasks are included in this work package.

ONGOING AND FUTURE WORK

WP 5.2 Status of on-going development tasks.

Task 5.2.1
The EUCAARI database is a modified interface accessing currently operational databases, EBAS (EMEP database) and ESA-CDB (Campaign Database, Envisat Cal/Val database). This approach is similar to the GEOmon project. For most measurements data is imported directly into the EBAS database. However, for complex measurements, such as air-borne LIDAR and RADAR, the ESA-CDB database may be utilized. Data incorporated into EBAS requires modified NASA-Ames format, while the CDB standard format is HDF. The systems will allow password protected access and work-flow functionality to create user access to certain datasets while keeping others restricted.

On-going work for the EUCAARI database includes: development of a new user management module, an automated data download monitoring tool that informs PIs of requests or downloads of their data, and direct connections to data-specific FLEXTRA trajectories and FLEXPART air mass histories. Furthermore, general stability of the web interface is continuously being improve toward the goal of implementing a stable operational system.

Task 5.2.2
We have conducted twenty day backward runs of the Lagrangian particle dispersion model FLEXPART for each of the EUCAARI stations at 3-hourly intervals. A suite of model output is available for the analysis of air mass histories at each station.

The products for EUCAARI are available from March 2006 and continue to through 2007 for most stations. For analysis of specific measurements, model output for each station is generated at six hour intervals (0, 6, 12, 18 UTC). There are 92 vertical layers in the input data. Calculations are based on an idealized inert tracer with an infinite lifetime allowing for interpretation of the results by a wide range of experimentalists. For each run numerous products are produced including plots at global, regional, and
local scale of the Potential Emissions Sensitivity (PES), Potential Source Contribution (PSC) for CO, NO2, and SO2, and a Retroplume Summary which provides an overview of the air mass pathway covering the previous 20 days from the date of interest.

Task 5.2.3
We are currently developing a dynamic browser for the viewing of FLEXPART products, the tool is being designed to ease navigation between measurement locations and time periods, as well as allow for quick comparison between database queries and transport model results. A preliminary version will be presented, but a complete system is not anticipated until early 2009.
INTRODUCTION

The aim of the EUCAARI 5.3 work package is to significantly improve the evaluation process of regional and global aerosol models and to document modeling progress made during EUCAARI. The evaluation will allow a quantification of actual uncertainties in our prediction of aerosol impact on climate and air quality. This will be achieved by evaluating not only the end product, but also important sub-steps in modeling. In this work package benchmark test tools shall be developed and applied, which allow analyzing model biases with respect to processes that govern aerosol concentrations and physico-chemical properties of the aerosol. The work package aims at developing a platform, which helps constructing successful modeling studies within EUCAARI and outside of the consortium. A subgoal of the work package is to achieve a link to the international AeroCom model intercomparison initiative (http://nansen.ipsl.jussieu.fr/AEROCOM).

ONGOING AND FUTURE WORK

Task 5.3.1 "Assessment of observational data base"

Data assessment involves that useful existing observational data are applied for model evaluation in cooperation with the scientists which have been preparing these data. This process is dependent on the type of data in question. In practical terms we call here the ‘observational data base’ those data which are and will be available for common model evaluation within EUCAARI in this work package. This assumes that they can be used directly in connection with the AeroCom tools on the AeroCom data server at the LSCE. To this date available data comprise sun photometer data from Aeronet, Skynet and GAW (1996-2007); satellite AOD and fine fraction of AOD from MODIS/CERES, MISR and POLDER/PARASOL (1996-2006); surface concentrations of major aerosol constituents, SO2, PM and sulfate wet deposition from EMEP, IMPROVE and CREATE (all years available); and Earlinet lidar data (2000+2001). Further work is under way to incorporate recent EUSAAR/EUCAARI intensive measurements when available, dry aerosol extinction from the GAW network, CALIOP lidar observations of aerosol extinction and selected meteorological data from the CRU database. Selected additional data will be added in the course of the development of the benchmark tests.

Task 5.3.2 “Development of pilot benchmark tests”.

Two benchmark tests have been developed in a pilot version: “Clear sky and all sky forcing”, “Aerosol size distribution”. These tests have been applied to the first simulations from the EUCAARI models and old model simulations being held in the AeroCom database. To make best use of the forthcoming
EUAARI model simulations we have also elaborated a set of “standard model diagnostics”, which need to be respected by modelers who wish to make use of the benchmark tests being developed.

In preparation of a systematic testing of different model components several preparatory steps had to be pursued in the course of the year. A standard diagnostics package was discussed among the EUCAARI partners and in the broader AeroCom community. Formatting tools for model output were coordinated with EUCAARI partners and with the international community involved in the preparation of new simulations for the next IPCC report. An AeroCom workshop was organised by the EUCAARI partners CEA, Univ Oslo and MPI-M in Iceland in October 2008.

The standard visualization tool of model data comparisons has been further developed in order to read directly standard model output without reformatting. The assessment now includes tables with scores reflecting the skill modeling or retrievals against reference datasets and additional visual aids illustrating comparisons of time series on daily, seasonal and annual resolution at all available stations and maps of observable quantities. Images are automatically transferred to a web interface as described below.

**Benchmark test « clear sky and all sky forcing »**

Two reference data sets have been assembled which are intended to serve as a benchmarks to judge new model results with respect to the direct radiative effect. The first reference are median fields of AeroCom Modeling (*AeroCom Median Model*), and the second reference is defined by results of off-line radiative transfer simulations with quality statistics of aerosol column properties by ground-based (sky-photometer) monitoring networks of AERONET and SKYnet (*Aeronet based gridded Aerosol Climatology*).

**AeroCom Median Model**

Relevant aerosol forcing parameters have been assembled in the form of an AeroCom model median that has been constructed from 12 models contained in the AeroCom database. Parameters included for clear sky conditions are emissions, column loads, total and anthropogenic aerosol optical depth, radiative forcing at the surface and at the top of the atmosphere, aerosol absorption optical depth, atmospheric column forcing. The individual model results are given in addition as a range of results. For all parameters sulphate, particulate organic matter and black carbon are singled out for more detailed comparison. Forcing efficiencies are computed as a function of optical depth, load and emission. See for example how the LMDzT-INCA result of total aerosol optical depth is situated against the background of other model simulations, observed AOD by AERONET, and an AeroCom Median model (figure 1).

---

**Figure 1:**

Aerosol optical depth at four sites characteristic for pollution, biomass burning, sea salt and dust. AeroCom A models are shown in grey, the AeroCom Median model in red and the Aeronet sun photometer Data in blue and the LMDzT-INCA model in green.
Aerocom-based gridded Aerosol Climatology

An observational based dataset of aerosol optical properties at high quality is provided by the ground-based sun-/sky photometer networks of AERONET and SKYnet. In constrast to aerosol remote sensing from space ground based transmission measurements, no a priori assumption of aerosol absorption or radiative background are necessary and all aerosol optical (and microphysical) properties can be consistently determined. Even though locally limited, over the past decade the sun-/sky-photometer data-bases provide solid statistics with at least one complete yearly cycle at more than 200 sites. For easier comparison to modeling (and satellite retrievals) the local ground-based statistics is merged onto a regular 1x1 (lat/lon) grid. Hereby, a site rating in employed to give sites with higher quality data and sites unaffected by local pollution or orography a stronger weight. Such gridded products (either for the multiannual average or for a particular year) provide test-beds for AOD, fine-mode fraction, Angstrom parameter, absorption optical depth and size (either effective radius or the complete size-distribution with 22 bins between radii of 0.05 and 15μm). For testbeds of aerosol direct effects (at ToA or surface) off-line radiative transfer simulation are conducted. And by excluding coarse mode aerosol sizes, in addition to the clear-sky forcing test bed also a clear-sky forcing test-bed for the fine size-mode can be developed.

Benchmark test « size distribution »

An initial testing of the size assumptions has been made by diagnosing the Angstroem component. As mode more solid tests is that of the fine fraction of the AOD. Reference data are the gridded AERONET products and possibly satellite data over oceans. While these indicators can help to identify problems, it is clear that they are insufficient to detect reasons for diversity in the specific model structure. It was thus decided in cooperation with partners from activity 3 to extend the diagnostics to a microphysics package. This includes in particular a request to modelers to output all model tracers at hourly or daily resolution at selected supersites. It also may involve AERONET sites with in highly detailed size-information. The specifications have been included in the standard model diagnostics package as described below.

Standard model diagnostics

Model diagnostics need to be fixed at an early point in time, because their implementation takes time and because model simulations can often not be repeated. Several diagnostic packages have been discussed during the AeroCom workshop in October 2008, which correspond to planned joint analysis and scientific problems. The definition of several diagnostic packages shall facilitate that modeling groups take up the work to implement the diagnostics. A summary is found in table 1 and more detail will be constantly updated on the AeroCom webpage (www.nansen.ipsl.fr/AEROCOM/protocol.html ). The exact formatting of model output is furthermore important to facilitate model intercomparison and joint evaluation. It has been agreed to fall back to the CMOR rewriting tool, developed by the PCMDI. An example program has been developed at the MPIM for treating ECHAM model output. The diagnostics as reported in table I have been standardized with respect to the CF naming convention of variables and netCDF attributes.

A part of the activities in WP3.4 is an intercomparison of the participating regional models for two specific cases representing distinctively different meteorological situations. The preparation of model output from regional models for incorporation into the test tools developed in this workpackage has been done in cooperation with the IFT partner. The primary goal here of formatting LM model output was to allow for a direct comparison to EARLINET lidar profiles. This work serves as preparation for model intercomparisons of the regional models participating in EUCAARI that will be integrated into the AEROCOM infrastructure. Such comparison is also expected to make a link to earlier work between the AeroCom community and the EARLINET lidar network.
<table>
<thead>
<tr>
<th>Diagnostic Package</th>
<th>Purpose</th>
<th>Content</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quicklook</strong></td>
<td>Allow quick evaluation via AeroCom tools of new model versions</td>
<td>For DUST, SS, BC, POM, SO4 Monthly: Emissions / 3D Loads / Wet&amp;Dry Deposition Daily: AOD speciated at 550+865 nm Full Coordinates</td>
</tr>
<tr>
<td><strong>Microphysics</strong></td>
<td>Size distribution and composition differences</td>
<td>Monthly 3D fields of all aerosol tracers (number+mass), H2SO4, NH3, SO2, DMS Aerosol water as well Formation rate of sulphate through processes, condensation sink Supersites hourly or daily: all aerosol tracer concentrations, dry and wet extinction, absorption</td>
</tr>
<tr>
<td><strong>Organics</strong></td>
<td>Document organic speciation and secondary organic aerosols, oxidants and semivolatilaty</td>
<td>MICROPHYSICS plus Monthly 3D fields BC, POM, SOA, O3, NOx, OH, NO3, OM/OC ratio Monthly 3D Formation rate of SOA, semivolatiles in gas/aerosol phase</td>
</tr>
<tr>
<td><strong>Vertical Distribution</strong></td>
<td>Constrain vertical mixing, wet removal and injection heights</td>
<td>TP1x for 2006 June 2006- 2007: Daily 3D speciated extinction/backscatter 532/1064 3D cloud cover (?10 lidar sites hourly extinction, RH, mass speciation, rad. fluxes ??)</td>
</tr>
<tr>
<td><strong>Dust emissions</strong></td>
<td>Understand differences in dust emission schemes</td>
<td>Dust emission modules in models, including maps and fortran code</td>
</tr>
<tr>
<td><strong>Direct Forcing</strong></td>
<td>New forcing estimate, Separate radiative effect calculation and aerosol cycle</td>
<td>2D: AS/CS SW TOA/SRF speciated forcing , cloudy sky forcing (SO4, BCFF, POMFF, BB, NO3, SOA), cloud cover 3D Surface Albedo=downward/upward SW at surface Asymmetry factor Absorption AOD, direct/diffuse CS, UVVis / NIR</td>
</tr>
<tr>
<td><strong>Indirect Forcing</strong></td>
<td>Investigate cloud-AOD relationships</td>
<td>see protocol IND2 CO2 + aerosol quasi forcing Fluxes in a run with fixed SST</td>
</tr>
<tr>
<td><strong>IPCC-aerosol</strong></td>
<td>Aerosol-climate effects and feedbacks</td>
<td>To be defined</td>
</tr>
</tbody>
</table>
A web interface to the EUCAARI model results has been attached to the standard AeroCom web interface. This allows to intercompare either the EUCAARI models among themselves and then to enlargen the comparison to other model results from the international community (http://nansen.ipsl.jussieu.fr/cgi-bin/AEROCOM/aerocom/surfobs_annualrs.pl?MODELLIST=EUCAARI). Different scores and statistics and visualizations are available via the web interface as mentioned above under the section benchmark tests.

Results from the initial testing of the EUCAARI model simulations have been made available over the summer and were discussed among participants during a joint EUCAARI-AeroCom workshop in October 2008 in Reykjavik/Island organized by the EUCAARI partners CEA, MPIM and Univ Oslo. The presentations from the workshop are available via the AeroCom web site (http://nansen.ipsl.jussieu.fr/AEROCOM/webreykjavik08.htm). A summary report from that workshop has been written and in the process of being reviewed. An important result from the workshop is a joint planning of model experiments among global aerosol modelers. Table II reports the major experiments foreseen in the next year. Note that a specific slot has been allocated for model simulations of the intensive EUCAARI experiment in 2008.

<table>
<thead>
<tr>
<th>Simulation Year(s)</th>
<th>Exp. Name</th>
<th>Description &amp; Diagnostics</th>
<th>Status/Submission</th>
</tr>
</thead>
<tbody>
<tr>
<td>1750+2000 or clim</td>
<td>IND2</td>
<td>Indirect effect</td>
<td>Ongoing / Nov 08</td>
</tr>
<tr>
<td>2001</td>
<td>HTAP-TP1x</td>
<td>Tracer experiments for HTAP, including soluble tracer</td>
<td>Ongoing</td>
</tr>
<tr>
<td>2004</td>
<td>HTAP-ICARTT</td>
<td>ICARTT campaign intensive</td>
<td>Ongoing</td>
</tr>
<tr>
<td>2006 (-2007)</td>
<td>A2</td>
<td>AeroCom Phase 2, Organics, Microphysics, Vertical, Quicklook, Direct Forcing</td>
<td>Ongoing March 09</td>
</tr>
<tr>
<td>1750+2000</td>
<td>B2fx+PRE2fx</td>
<td>Prescribed forcing, Direct Forcing</td>
<td>March 09</td>
</tr>
<tr>
<td>1750+1980-2007</td>
<td>HCA-0</td>
<td>Hindcast daily &amp; monthly</td>
<td>Ongoing</td>
</tr>
<tr>
<td>1750+1980-2007</td>
<td>HCA-IPCC</td>
<td>Hindcast daily &amp; monthly</td>
<td>July 09</td>
</tr>
<tr>
<td>2008</td>
<td>A2 prolonged</td>
<td>Organics, Microphysics</td>
<td>Oct 09</td>
</tr>
<tr>
<td>1750+1980-2007</td>
<td>HCA-MET</td>
<td>Hindcast monthly</td>
<td>Oct 09</td>
</tr>
<tr>
<td>1750+1980-2007</td>
<td>HCA-FX</td>
<td>Hindcast monthly</td>
<td>Oct 09</td>
</tr>
<tr>
<td>1860-2100</td>
<td>IPCC</td>
<td>IPCC-aerosol</td>
<td>Mid 10</td>
</tr>
</tbody>
</table>
A subset of EUCAARI models has also participated in the HTAP model intercomparison exercise. Both LMDzT-INCA and ECHAM model results have been reported to the HTAP/AeroCom model database. A first specific evaluation of the aerosol transport simulations to the Arctic has been published recently (Shindell et al., 2008). The evaluation shows clearly that the current diversity among models for long range transport of partly soluble substances such as black carbon and sulphate is a major source of uncertainty for anthropogenic aerosol loads.

REFERENCES

SIZE DISTRIBUTION OF TOTAL CARBON AND SULFATE CONCENTRATION IN BACKGROUND AEROSOL, HUNGARY

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Keywords: fine mode aerosol, seasonal variation, carbon-sulfate ratio, water soluble organic carbon

INTRODUCTION

In the last decades the role of aerosol particles in atmospheric processes has been studied worldwide. Aerosol particles affect the radiation budget of the Earth-atmosphere system directly; and they control the cloud formation as well as the optical properties of the clouds. The role of the particles in visibility regulation is also of great importance (DeBell et al., 2006). It is well known that these processes depend on the size and on the chemical composition of the particles. Beside inorganic constituents, carbon containing species give the most important fraction of atmospheric aerosol in the fine particle size range. The results obtained during the last decade show that considerable part of these species is water soluble. Recently the effect of organic material on aerosol activation is in the focus of considerable attention (Varga et al, 2007).

Since the above mentioned processes are controlled mainly by the fine particles, in this work the size distributions of inorganic ions (sulfate and nitrate) and carbonaceous (total carbon, water soluble carbon) compounds are presented for the fine mode aerosol. On the other hand, the seasonal variation of these components is discussed.

EXPERIMENTAL

The aerosol sampling was performed at the Hungarian background air-pollution monitoring station at K-puszta. The samples were collected on weekly basis in 2008, from January to June. The sampling site is located on a forest clearing on the Great Hungarian Plain, approximately in the middle of the country. The average height of the region around the station is 125m a.s.l. Sampling was carried out by an electrical low pressure impactor (ELPI). The air was sampled at a height of 10m above the surface, under ambient temperature and humidity conditions. The flow rate through the sampler was 26.4lmin⁻¹, the lower cut-off diameters of stages were 0.03, 0.06, 0.11, 0.18, 0.27, 0.42, 0.68, 1.05, 1.70μm.

Additionally, results on water soluble organic carbon are also involved in this study. These data, however, came from different sampling period (January-April, 2007). The sampling site was also K-puszta, while for sample collection a 9-stage Berner impactor was applied. The flow rate was 31.3lmin⁻¹, the lower cut-off diameters of stages presented in this work were 0.03, 0.06, 0.11, 0.18, 0.27, 0.42, 0.68, 1.05, 1.70μm.

In all cases the samples were collected on aluminum foils and they were stored in the freezer until analysis. The aerosol samples of different size ranges were chemically analyzed. Measurements of total carbon (TC) and water soluble carbon (WSOC) were carried out by using an Astro Model 2100 TOC solid-analyzer. The concentrations of total carbon and WSOC were measured as carbon dioxide by a catalytic combustion method in oxygen at 680°C. The detector response was calibrated with standard solutions of potassium hydrogen phthalate. The detection limit of carbon measurements was 0.7 mg C
The concentrations of sulfate and nitrate were determined by ion chromatography. The detection limits of the inorganic ion concentrations were <100 µg l⁻¹ (Imre and Molnár, 2008).

RESULTS

The results in Fig. 1 show that in the fine size range sulfate (except in summer), nitrate and TC were characterized by bimodal size distributions. The highest concentrations were found in the droplet mode, while a second peak was obtained in the condensation mode, with geometric mean diameters of 0.53 and 0.28µm, respectively. These two modes indicate that in the majority of cases at K-puszta aged aerosol can be measured. However, in summer, in the size distribution of sulfate three modes could be distinguished. The third peak appeared below 0.1µm, showing the evidence of new particle formation. The size distribution of WSOC had almost the same feature, the maximum concentration was found in the droplet mode. WSOC/TC ratio, however, showed important size dependence. For particles smaller than 0.1µm the share of WSOC was around 100% both in winter and in spring, while with increasing particle size the contribution of WSOC to TC decreased significantly.

Figure 1. Seasonal variation in the size distribution of different aerosol compounds at K-puszta.

In the size distributions of the compounds important seasonality could be observed. The lowest nitrate concentration was found in summer, due likely to the volatility of NH₄NO₃. Nitrate/sulfate ratio may indicate the importance of nitrate compared to sulfate ions (see Table 1). The seasonal changes in the nitrate concentration are clearly shown by this ratio. In winter the nitrate/sulfate ratio is high around 1, meaning that nitrate concentration was comparable to sulfate concentration. On the other hand in spring and summer this ratio generally decreased and showed slight size dependence.

Seasonal variation of sulfate concentration was not found very important. This year the highest concentration was measured in winter probably due to stable atmospheric conditions. Earlier measurements (Temesi et al., 2003) showed that sulfate concentrations had summer maximum attributed to high photochemical activity in summer. The direct relationship between sulfate production and
photochemical activity has already been demonstrated in several works. The photochemical activity on sulfate production could be followed when sulfate size distributions in spring and summer are compared (see Fig. 1).

Total carbon (TC) content of the fine particles was found to be important in all seasons. Similar to nitrate, TC concentration was significantly higher in winter than in spring or summer. To compare the possible role of sulfate and organic particles in different size ranges, the values of carbon/sulfate ratio were calculated. Data in Table 1 show that, in accordance with our earlier results (Temesi et al., 2003), in every size ranges the carbon concentration exceeds the sulfate concentration, except in summer. In summer the amount of sulfate is higher than TC concentration in the 0.22–1.34 μm size range. From these data it is also obvious that ultrafine particles also contained high amount of carbonaceous components.

WSOC concentration can be regarded more or less constant during the year, as it was also shown by our earlier observations (Temesi et al., 2003). In spring and winter the total fine mode WSOC concentrations were 1.08 and 0.78 μgm⁻³, respectively, the contribution of fine mode WSOC to the total WSOC content was found 67% in both seasons. However, contrary to the other constituents presented in this work, WSOC concentration increased from winter to spring. It is speculated that this increase can be attributed to the increase of photochemical activity.

<table>
<thead>
<tr>
<th>Geometric mean diameter (μm)</th>
<th>nitrate/sulfate</th>
<th>TC/sulfate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>winter spring summer</td>
<td>winter spring summer</td>
</tr>
<tr>
<td>0.04</td>
<td>0.68 0.53 0.42</td>
<td>1.01 0.85 0.97</td>
</tr>
<tr>
<td>0.08</td>
<td>0.78 0.59 0.10</td>
<td>1.72 1.05 0.29</td>
</tr>
<tr>
<td>0.14</td>
<td>0.86 0.54 0.21</td>
<td>2.21 1.36 1.64</td>
</tr>
<tr>
<td>0.22</td>
<td>1.09 0.77 0.13</td>
<td>2.92 1.41 0.60</td>
</tr>
<tr>
<td>0.34</td>
<td>1.02 0.56 0.12</td>
<td>2.43 1.15 0.48</td>
</tr>
<tr>
<td>0.53</td>
<td>1.45 0.97 0.33</td>
<td>1.82 1.02 0.34</td>
</tr>
<tr>
<td>0.84</td>
<td>1.25 0.74 0.26</td>
<td>1.33 0.97 0.37</td>
</tr>
<tr>
<td>1.34</td>
<td>1.02 1.27 0.42</td>
<td>0.98 0.63 1.14</td>
</tr>
</tbody>
</table>

REFERENCES


Influence of experimental conditions on particle formation starting from OH + SO$_2$

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For more than a decade the formation of new aerosol particles in the atmosphere has been the subject of intense studies in the field and in the laboratory. The formation mechanisms and the participating substances, however, have not been resolved yet (Kulmala, 2003). Large discrepancies between model-predicted nucleation rates for the favored binary system H$_2$SO$_4$/H$_2$O and much higher atmospheric nucleation data were explained by various supportive additional participants such as NH$_3$ (Kulmala et al., 2000) or organic molecules (Hoffmann et al., 1998). Modeling studies predict an enhancement of binary H$_2$SO$_4$/H$_2$O nucleation rate by several orders of magnitude for NH$_3$ mixing ratios > 1ppt (2.5 $\times$ 10$^{-7}$ molecule cm$^{-3}$) (Korhonen et al., 1999). Subject of this experimental study is the role of NH$_3$ in the process of new particle formation starting from OH + SO$_2$.

The experiments have been performed in the atmospheric pressure flow-tube IfT-LFT (i.d. 8 cm; length 505 cm) at 293 $\pm$ 0.5 K (Berndt et al., 2005). Gas-phase analysis was carried out using photo-acoustic spectroscopy for NH$_3$ (OMNISENS: TGA 310), gas analyzers for O$_3$, SO$_2$, and NO$_x$ (Thermo Environmental Instruments: 49C, 43C, and 42S), a butanol-based UCPC (TSI 3025) as well as a H$_2$O-based UCPC (TSI 3786) for integral particle measurements, and a differential mobility particle sizer (Vienna-type DMA with UCPC, TSI 3025) for monitoring of size distributions. The carrier gas consisted of synthetic air (99.9999999 %, Linde and further purification with Gate Keeper, AERONEX).

Using the NH$_3$ analyzer TGA 310, the carrier gas NH$_3$ concentration was below the stated detection limit of 0.1 ppb (2.5 $\times$ 10$^{-9}$ molecule cm$^{-3}$). Generally, it is hard to measure and to handle NH$_3$ concentrations $<$ 10$^{10}$ molecule cm$^{-3}$ caused by the high solubility of NH$_3$ in water and the resulting memory effects due to the presence of wetted surfaces (reactor walls, transfer lines, etc.). So it seems to be impossible to exclude (or to perform experiments with) NH$_3$ mixing ratios $\sim$1ppt (2.5 $\times$ 10$^7$ molecule cm$^{-3}$) as postulated to be sufficient for ternary nucleation H$_2$SO$_4$/NH$_3$/H$_2$O (Korhonen et al., 1999). In the experiments presented here the added NH$_3$ concentrations were a few 10$^{10}$ - 10$^{12}$ molecule cm$^{-3}$, i.e. in the range of atmospheric levels or a bit higher. In order to evaluate the wall loss in the IfT-LFT NH$_3$ measurements have been performed at the entrance to the flow tube as well as at the outlet port. Figure 1 shows typical experimental findings:

![Figure 1: Detected particle number (TSI 3025) as a function of "H$_2$SO$_4$" with and without added NH$_3$ for different r.h. "H$_2$SO$_4$" stands for all SO$_2$ oxidation products. Bulk residence time: 42 sec.](image_url)

The influence of NH$_3$ on the formation of new particles was studied varying the residence times in the IfT-LFT, the humidity in the system and using different NH$_3$ concentrations. Furthermore, first results from measurements describing the real number of new particles as a function of "H$_2$SO$_4$$" and relative humidity are reported.

EVALUATING NEW PARTICLE FORMATION MECHANISMS USING A GLOBAL AEROSOL MODEL AND GLOBAL CN DATA

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Keywords: aerosol, nucleation, global model

INTRODUCTION

Particle formation in the boundary layer has been extensively observed and simulated at local scales. These studies have used particle formation events to derive empirical mechanisms relating the nucleation rate to the concentration of sulphuric acid vapour. So far, the evaluation of these mechanisms has been limited to very few locations in Europe and the US. Here, we use a global aerosol model and observations of total particle number (CN) from worldwide surface stations to test different formation mechanisms in the boundary layer. The results provide strong evidence for the importance of nucleation as a global source of particles.

RESULTS

We compare long term observations of aerosol particle number at 12 surface locations (CREATE and WDCA datasets) with results from the Global Model of Aerosol Processes (GLOMAP). The results are shown in Fig 1.

Figure 1. Monthly mean CN concentrations (black symbols) compared with the global model assuming different boundary layer nucleation mechanisms. Black line – primary emissions only. Red lines - \( J_{10} = k[H_2SO_4] \) with various rates. Blue lines - \( J_{10} = k[H_2SO_4]^2 \) with various rates.
At polluted continental sites primary anthropogenic emissions can potentially explain the majority of observed particle number, whereas at remote continental sites increasing the primary anthropogenic emission rate by a factor of 10 does not match observed aerosol number. We evaluate two empirical nucleation mechanisms where the formation rate of 1 nm particles \( J_1 \) is based on sulfuric acid concentrations \([\text{H}_2\text{SO}_4]\) to the power of 1 or 2. At remote locations particle formation accounts for 40-90% of observed particle number. Both the activation \( J_1=A[\text{H}_2\text{SO}_4] \) and kinetic nucleation mechanisms \( J_1=k[\text{H}_2\text{SO}_4]^2 \) equally explain observations improving the \( R^2 \) between simulated and observed monthly mean aerosol number across all sites from 0.32 without particle formation to 0.63 and 0.62 respectively.

By matching observed and simulated total particle number we calculate the best fit global value of \( A \) and \( K \) to be \( 2 \times 10^{-6} \text{ s}^{-1} \) and \( 1 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) respectively, in line with previous calculations based on observations of individual new particle formation events. However, using vertical profiles of aerosol number observed over Europe and the United States we show that both these mechanisms overpredict particle number in the free troposphere (2-8 km) by up to a factor of 5, unless the mechanisms are restricted to the boundary layer. In addition, total particle number over the North Atlantic ocean is also overpredicted by more than a factor of 3 unless the mechanism is restricted to continental regions. This analysis suggests that particle formation depends on variables additional to sulfuric acid that are coincident with continental surface regions.

ACKNOWLEDGEMENTS

This work was funded by the EUCAARI Integrated Project and the Natural Environment Research Council in the UK.
INTRODUCTION

New particle formation has been recognized to represent a significant source of cloud condensation nuclei (CCN) worldwide (Kulmala 2003). Considerable efforts have been spent to understand the mechanisms responsible for the nucleation and growth of new atmospheric particles as well as the environmental factors favouring or inhibiting them. For instance, the probability of new particle formation is reduced in a polluted atmosphere due to the high levels of pre-existing particles acting as condensation sink for the precursors of incipient particles. In spite of that, a frequency of around 130 days with clear new particle formation events per year has been observed in the Po Valley, one of the most polluted area in Europe (Laaksonen et al., 2005; Hamed et al., 2007). In the past studies at the rural station of San Pietro Capofiume, in the central-eastern part of the valley, it was found that the frequency of nucleation in spring and summer is two to three times higher than in winter, and that temperature, wind speed, solar radiation, SO$_2$ and O$_3$ concentrations were correlated with the frequency of nucleation, while relative and absolute humidity and NO$_2$ were anticorrelated with it (Hamed et al., 2007). However, the same study showed that the environmental variables identified for other geographical sites where nucleation has been observed were not fully successful for describing the phenomenology of new particle formation in the Po Valley.

A new field experiment was conducted at the same field station in San Pietro Capofiume from 31 March to 20 April 2008 in the frame of the EUCAARI project. During the experiment, an unprecedented suite of instruments for ground-based aerosol and gas measurements was operating continuously at the site providing a new insight to mechanisms underlying the formation of new particles in the Po Valley.

METHODS and RESULTS

Aerosol measurements included:
- In situ (on line) systems: BSMA, twin-DMPS, CPC, CCN, V-TDMA, VH-TDMA, UFO-TDMA, Q-AMS, wTOF-AMS, PSAP, nephelometer, OPC;
- In situ (off line) systems: multistage impactors, PM$_1$ daily filters, HiVols and dichotomous (PM$_{10-1}$ and PM$_1$) sampler for off-line inorganic and organic analyses by EGA, liquid-TOC, IC, IC-MS, and $^1$HNMR spectroscopy;
- Remote sensing systems: lidars, photometer.

Gas measurements were carried for NH$_3$ (with wet denuders), SO$_2$, O$_3$, NO, NO$_2$. 
The preliminary results from twinDMPS, AMS, lidars and wet denuders show that new particle formation occurred in the late morning when the continental boundary layer developed causing the dilution of the aerosol-rich nocturnal surface layer. In less than an hour, the concentration of pre-existing particles experienced a ten times decrease, and freshly-formed ultrafine particles appeared readily. We hypothesize that the fast development of a thick continental boundary layer promotes new particle formation by allowing: a) a marked decrease of the condensation sink, b) the vertical mix of precursors previously segregated in the stratified atmosphere of the night and early morning. Possible precursors include ammonia, which accumulates near the surface during the night until the early morning, together with amines. The latter could not be directly measured in the gas phase, but they were found condensed in the nocturnal aerosol, with monomethyl-, dimethyl-, trimethyl-, and triethyl-amines as most important species identified by 1HNMR analysis. We hypothesize that the development of the boundary layer allows these alkaline species to react with acidic gases in the aloft layers, promoting new particle formation. These findings strongly support the importance of chemical mechanisms in addition to environmental variables in explaining the nucleation events in a polluted atmosphere.

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Figure 1. New particle formation event in San Pietro Capofiume on 04 April 08. a) evolution of the particle number size distribution from twin-DMPS; b) lidar (LD-40) profile with white dots indicating stratifications in the aerosol distribution; c) mass concentrations of major aerosol chemical compounds from w-TOF-AMS; d) gaseous ammonia concentrations from wet denuders (AMANDA). The lidar profile is shifted of one hour with respect the other panels because of the difference between the time scales used (UTC instead of UTC+1).
SECONDARY ORGANIC AEROSOLS FORMATION FROM ANTHROPOGENIC AND BIOGENIC SOURCES: BRIDGING FIELD AND SMOG CHAMBER EXPERIMENTS

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Keywords: secondary organic aerosol, chemical composition, nuclear magnetic resonance spectroscopy.

INTRODUCTION

Secondary Organic Aerosol (SOA) account for a substantial fraction of total organic particulate mass and is formed in the atmosphere by the photochemical processing of gaseous precursors emitted from both biogenic and anthropogenic activities. Although on a worldwide basis biogenic Volatile Organic Compounds (VOCs) are the most important source of SOA, in urban areas VOCs emitted from anthropogenic sources often dominate. In order to obtain an accurate prediction of atmospheric SOA it is essential to clarify the most important SOA forming reactions. So far, most studies have focused on SOA yields per unit of gaseous precursor concentration, while the knowledge of the chemical composition of SOA in different environments and its dependence on ambient conditions is still rather limited.

Here we present new results of chemical characterization of SOA produced in smog chambers by biogenic and anthropogenic gaseous precursors and compare them with the results obtained on selected ambient SOA samples.

METHODS AND RESULTS

In the framework of the projects EUCAARI and PolySOA, laboratory-SOA were produced in the SAPHIR and PSI smog chambers by a series of photooxidation experiments using α-pinene, or mixtures of monoterpenes (MT), or monoterpenes with sesquiterpenes (SQT) as models for biogenic emissions and 1,3,5-trimethylbenzene (TMB) as a typical anthropogenic precursor. Furthermore laboratory-generated SOA composition was investigated in different ranges of precursor concentrations (20-60 μg/m³ and 60-200 μg/m³). Ambient SOA samples were collected in both pristine and polluted environments during joint measurements campaigns held in the frame of the project EUCAARI in the Finnish boreal forest (Hyytiala) and in the Po Valley (Italy).

A suite of spectroscopic and chromatographic methods were employed to investigate the chemical composition of SOA collected on various filter substrates. The analytical methods included determination of Total Carbon (TC) and Water-Soluble Organic Carbon (WSOC), the speciation of WSOC into main chemical classes on the basis of their acidic properties and characterization of WSOC by Proton Nuclear Magnetic Resonance (1H-NMR) spectroscopy for functional group analysis.

As expected, laboratory-generated SOA are mainly composed by polar (water-soluble) compounds. Results indicate that chamber SOA formed in high (60-200 μg/m³) concentration experiments show a more polar composition with respect to low (20-60 μg/m³) concentration SOA which contain a significant fraction of water-insoluble compounds. Anion exchange liquid chromatography (HPLC) coupled to a TOC analysis was exploited for quantitatively resolving water-soluble organic compounds in the following main chemical classes: neutral compounds, mono- and di-acids, and polyacids, the latter including humic-like substances (HULIS). As for biogenic SOA, in both laboratory-generated as well in ambient samples the water-soluble fraction is composed mostly of neutral compounds and monocarboxylic acids with a
much lower contribution of dicarboxylic acids and HULIS. 1,3,5-trimethylbenzene laboratory generated SOA show a substantially different contribution of acidic compounds compared to anthropogenic ambient SOA.

The distribution of major functional groups present in water-soluble fraction of the aerosol was provided by 1H-NMR (i.e. extracts were dried and re-dissolved in a small volume of D$_2$O for 1H NMR analysis at 400 MHz with methanol as internal standard). In the Figure 1 the spectral signatures of biogenic SOA collected in ambient and produced in smog chamber experiments are shown. The spectral features of biogenic laboratory SOA fit fairly well those of biogenic ambient SOA collected in Hyytiala, reproducing both the occurrence of semi-volatile species such as pinic and pinonic acids as well the background signal attributable to a more complex mixture of degradation products. When the concentration of the gaseous precursor in the chamber is lower, closer to ambient condition, the resulting spectra is more similar to that of biogenic ambient SOA since the contribution of the sharp peaks becomes less pronounced with respect to the background signal.

Fewer common characteristics emerge from the comparison of 1,3,5-trimethylbenzene and polluted SOA. The TMB spectra present a chemical composition prevalently aliphatic with a lower contribution of species containing oxygenated groups (ketones or carboxyls) as compared to ambient polluted SOA. Aromatic and hydroxilated groups contribute significantly to the ambient SOA composition while their concentration is much lower in the laboratory-generated SOA. Polluted ambient samples show a larger complexity pointing to the contribution of additional precursors. Clearly, the SOA produced from 1,3,5-trimethylbenzene are unable to reproduce the content of oxygenated functional groups observed in ambient samples, calling for investigating alternative anthropogenic SOA precursors or suggesting a contribution of oxidized organic compounds from different sources, such as biomass burning.

H-NMR spectroscopy, providing integral chemical properties of the organic mixtures, represents a valuable tool to link laboratory and ambient SOA and can help to design future smog chamber experiments under realistic conditions for SOA formation.
Fig. 1 Starting from the top of the figure are shown 1H-NMR spectra of SOA produced in the SAPHIR chamber from the photooxidation of mixtures of monoterpenes and sesquiterpenes (MT+SQT). SOA collected at the beginning and at the end of the photooxidation experiment are labelled as fresh and aged SOA respectively. A spectrum obtained from α-pinene during a low-concentration experiment in the PSI chamber (POLYSOA campaign) is added for comparison. Finally, a spectrum of a PM1 sample collected in Hyytiälä during the EUCAARI experiment in April 2007 is reported on the bottom.

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GLOBAL AEROSOL MODELLING
FOR THE INTENSIVE LONGREX & IMPACT FIELD CAMPAIGNS
IN THE FRAMEWORK OF EUCAARI PROJECT

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Keywords: aerosol, global and regional modelling

INTRODUCTION

Atmospheric aerosols play an important role in the global climate system. They modify the global radiation budget directly, by scattering and absorption (McCormic and Ludwig, 1967) and indirectly, by their interaction with clouds (Twomey 1974, Albrecht 1989). The quantitative evaluation of the aerosol effects is still uncertainties (Kinne et al., 2005) both for the complexity of the global aerosol system and the short aerosol lifetime which causes large spatiotemporal inhomogeneities. Though in situ observations represent the most detailed insight into the aerosol system, they have limited spatial and temporal scales. Remote sensing data from ground-based instruments provide important information but they have sampling limitations as well. Then, satellite data only provide integral aerosol properties and retrievals rely on a priori information about the aerosol system and internal aerosol models.

Global aerosol models can help to increase the understanding of the complex aerosol system for past, present and future conditions. Moreover, it is possible to identify the effects of specific aerosol components and aerosol sources on the climate system.

The EUCAARI (European Integrated project on Aerosol Cloud Climate and Air Quality Interactions) is designed to bridge the scales through connected activities beginning at molecular scale (Monte Carlo and Molecular Dynamics to understand nucleation and aerosol thermodynamic processes) and finishing at the regional and global scale (Global Climate and Air Quality simulations to understand transport and deposition processes and improve numerical models via novel parameterizations).

Our global aerosol modelling objectives in EUCAARI are:

- A broad model evaluation against observations through the integration of new in situ, ground-based, remote and satellite observations.
- Use of new emissions inventories and new processes.
- Model microphysics evaluation using benchmark datasets with the aim of producing the most accurate schemes for the least computational cost.
- Ultimately, improvements in global and regional process models will be used to evaluate the reliability of highly parameterised schemes used in global climate models, with improvements made as necessary.

Two intensive field campaigns were performed inside EUCAARI: LONGREX and IMPACT. EUCAARI-LONGREX (LONG Range EXperiment) is an aircraft field campaign conducted in May 2008. The experiment aimed to measure the aerosol distribution over Europe by airborne in-situ and remote sensing measurements on a rather large scale. During EUCAARI-LONGREX two extensively equipped research aircraft, the DLR Falcon 20 and the FAAM BAe-146 were operated out of Oberpfaffenhofen in southern Germany. The aircraft flew mainly West-East and North-South transects across Europe in order to follow the evolution of aerosol properties during air mass transport over Europe.
EUCAARI-IMPACT, more focused on understanding the link between aerosol and clouds and thus the indirect effect of aerosols took place in May 2008 at Cabauw, the Netherlands. A great variety of air masses come across this region depending on air mass history. The campaign was designed to both observe clouds and aerosols and therefore to investigate the aerosol indirect effect.

AEROSOL MODELLING: GLOMAP MODEL

Due to the complexity of aerosol microphysics, global climate models generally only simulate aerosol mass and assume size distributions for the aerosol depending upon the composition. Sectional schemes resolving the size distribution of aerosol are often computationally expensive and therefore not suitable for inclusion within global circulation model (GCM). Aerosol can be represented by log-normal distribution scheme with a reduced computational time but with a priori assumption on the size distribution.

The GLObal Model of Aerosol Process (GLOMAP, Spracklen et al., 2005) has the unique advantage of having two aerosol schemes: a sectional (bin) scheme (referred as GLOMAP-bin, hereinafter) and a log-normal modal scheme (referred as GLOMAP-mode, hereinafter). Therefore, it is a useful tool to test how well a less computationally expensive modal scheme is able to represent aerosol compared with a bin scheme and meet the challenge of multi-scale integration in EUCAARI.

GLOMAP is based on the TOMCAT chemical transport model and simulates the emission, processing and deposition of sulphate, sea salt, black carbon and organic carbon aerosol. Fig. 1 shows a scheme of the model.

![GLOMAP Scheme](image)

**Figure 1. GLOMAP scheme**

GLOMAP-bin uses a sectional scheme (20 bins, spanning a range from 1 nm to 25 um) carrying both mass and number. GLOMAP-mode uses 7 lognormal modes defined in terms of number and masses of each chemical component. The mode spread (defined as the geometric standard deviation) is fixed with independent values for each of the modes within the model. GLOMAP-mode has been developed for use in the UK Met Office Unified Model (UM) as part of the new UK Chemistry and Aerosol (UKCA) sub-model. Both models use identical emissions and comparable process descriptions, although the implementation is changed where necessary.
SETUP OF THE SIMULATIONS

The aerosol fields in GLOMAP are generated from an initially aerosol free atmosphere. For the simulations in this work, the model has been 'spun-up' for a 3-month simulation time to allow the processes of emission, processing and removal to produce a realistic aerosol distribution.

The GLOMAP-bin simulation contains two distributions and five aerosol types. Both distributions contain 20 bins with the bin centres spaced geometrically across a size ranges of 1nm to 25 μm. The first distribution contains black carbon (BC), organic carbon (OC) and secondary organic aerosol (SOA) and is assumed to be insoluble. The second (soluble) distribution contains sulphate, sea-salt and aged BC and OC aerosol. The GLOMAP-mode simulation contains five modes and five aerosol components. Modes included are nucleation, Aitken, accumulation and coarse soluble as well as the insoluble Aitken mode. Sulfate, sea-salt, black carbon, organic carbon and secondary organic carbon aerosols are included within the soluble modes. Black carbon and organic carbon are emitted into the insoluble modes and may be aged through condensation of H₂SO₄, heterogeneous oxidation of SO₂ or coagulation with soluble aerosol.

The GLOMAP runs include primary aerosol emissions from natural sources, anthropogenic sources and wildfire sources. In the simulation of secondary particle production, we attempt to explicitly simulate the competition between nucleation of new particles and the condensational growth of pre-existing aerosol. New particle nucleation is parameterised following Kulmala (1998) which describes the binary nucleation of sulfuric acid and water.

Emissions of Sulfur species include anthropogenic and volcanic emissions of SO₂ and oceanic emissions of DMS. Oxidant fields (OH, H₂O₂, HO₂ and NO₃) are climatological 6 hour monthly means from a full TOMCAT tropospheric chemistry run. Convective & large-scale precipitation and low cloud products used to diagnose cloud fraction for in-cloud processing of aerosol are calculated from the ECMWF meteorological analyses.

To better compare against observations, during the LONGREX and IMPACT intensive field campaigns, GLOMAP was setup to provide output each hours over a regional (European) domain (Fig. 2). All the results in the present work have a horizontal resolution of 2.8 x 2.8 degrees and 20 vertical levels from surface to 10 km.

Figure 2. GLOMAP setup for the intensive LONGREX and IMPACT field campaigns. In addition to the standard output (daily average over the global domain), hourly outputs over a regional (European) domain were setup.
PRELIMINARY RESULTS

A wide evaluation of the model against observations is required as first step before looking for possible discrepancies and then improve the model via novel parameterization.

Both during LONGREX and IMPACT, the sample database was extremely interesting from a modelling point of view. An anticyclonic system dominated Europe during the campaigns and brought clear skies and high pollution loading. Many different aerosol types were sampled and many aerosol physical and chemical processes can be investigated through the model, like ageing of particles during the transport, particles formation and condensation onto existing particles from precursor gases originating from pollution and natural sources; cloud processes; exchange between polluted boundary layer and clean free troposphere. This important dataset will be used to develop and test new parameterisations of aerosol formation, transformation, optical properties, and interaction with clouds, including sub-grid scale effects.

Fig. 3 show an example of model/observations comparison. The output of the model was 3D interpolated along the flight-path of the aircraft. The graph shows the timeseries of sulphate for the flight on May 6. This flight aimed to sample pollution outflow from Central Europe towards UK and Northern Sea. The agreement between the two models is quite good (differences are less than 0.3 \( \mu g/m^3 \)) along all the flight-path while differences against AMS observations are about 1 \( \mu g/m^3 \).

Figure 3. Time series of the sulphate for the flight on May 6. The red lines is the AMS data, the blue line is sulphate from GLOMAP-bin and the green line is sulphate from GLOMAP-mode.

Fig. 4 show the distribution of BC mass concentration over Europe from GLOMAP-mode at 0.03 and 1.3 km. The black line indicates the trajectory of the aircraft.
Figure 4. European distribution of black carbon mass concentration from GLOMAP at 0.03 and 1.3 km on May 6. The black line indicates the trajectory of the aircraft.

Fig. 5 and 6 show the comparison of BC mass from GLOMAP and from observations at Cabauw station (with aethalometer) and along the flight-path of the aircraft (with SP2 instrument) on May 6. At Cabauw station (Fig. 5) the model seems to systematically underestimate the black carbon mass (background values between 350-450 ng/m³ against 650-750 ng/m³, apart from the peak observed between 4 and 10am probably due to local pollution). The underestimation of the model is not shown against BC from SP2. Systematic differences are shown between the two models (BC from GLOMAP-mode higher than BC from GLOMAP-bin; differences are about 20 ng/m³) which need more investigations.

Figure 5. Black carbon mass concentration at Cabauw station from aethalometer (lines) and from GLOMAP (blue circles)

Figure 6. Black carbon mass concentration along the BAe-146 flight-path from SP2 (red line) and from GLOMAP-bin (blue line) and GLOMAP-mode (red line)

SUMMARY & CONCLUSIONS
This work presents a preliminary analysis of the aerosol distribution over Europe during the intensive EUCAARI and LONGREX filed campaigns. The preliminary results can be summarized as follows:

- GLOMAP model is a useful tool to understand
- The database collected during the intensive LONGREX and IMPACT field campaigns are extremely interesting and can potentially improve the model parameterizations.
- First comparisons between model and observations are encouraging, though a wide-range observations need to be used to quantify how are the skills of the model to predict the aerosol size distribution and chemical composition over Europe.

ACKNOWLEDGMENTS

This work is supported by the European Commission under the EUCAARI project and the Natural Environment Research Council ADIENT project. The authors would thank all groups and the Institutions inside LONGREX and IMPACT campaigns for providing data.

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Aerosol plays a significant role in affecting the radiative budget of the Earth as a result of scattering and absorption of solar radiation and via interaction with clouds (Haywood and Boucher, 2000). The processes of scattering and absorption directly affect the radiation balance by changing the portioning of energy between the surface and the atmosphere. Certain aerosol act as cloud condensation nuclei (CCN) causing them to indirectly affect the climate by changing cloud brightness and lifetime (Lohmann and Feichter, 2005). Aerosols are one of the greatest sources of uncertainty in interpretation of climate change of the past century and in the projection of future climate change (IPCC 2007). However, large uncertainties exist in current estimates of aerosol radiative forcing because of the incomplete knowledge concerning the distribution and the physical and chemical properties of aerosols as well as aerosol-cloud interactions (Yu et al., 2006). Critical to this calculation are aerosol optical properties (aerosol optical depth, single scatter albedo, phase function). Understanding the radiative effects of aerosol is strongly related to the understanding of the microphysics that governs the aerosol processes. The modelling of aerosol is crucial to improving the understanding of the key microphysical processes that drive the interaction with radiation and clouds. In this work we present preliminary results comparing modelled aerosol optical depth (referred as AOD, hereinafter) from GLOMAP and observed AOD from AERONET stations over Europe during the intensive LONGREX and IMPACT field campaigns in the framework of EUCAARI (European Integrated Project on Aerosol Cloud Climate Air Quality Interaction) and ADIENT (Appraising the Directs Impacts of Aerosols on Climate) projects. We use two different aerosol microphysics schemes, one based on a sectional size distribution and the other on a computationally faster modal distribution. One aim of this comparison is to determine the level of model sophistication required to capture the observations and therefore contributes to WP3.3 in Development of Parameterisations.

AEROSOL MODELLING: GLOMAP MODEL

GLOMAP is based on the TOMCAT chemical transport model and simulates the emission, processing and deposition of sulphate, sea salt, black carbon and organic carbon aerosol. Fig. 1 shows a scheme of the model. Two versions of GLOMAP (GLOMAP-bin and GLOMAP-mode) are available which differ in the way they treat the size distribution. GLOMAP-bin model uses a comprehensive sectional scheme (20 bins, spanning a range from 1 nm to 25 um) carrying both mass and number. GLOMAP-mode model uses 7 lognormal modes defined in terms of number and masses of each chemical component. The mode spread (defined as the geometric standard deviation) is fixed with independent values for each of the modes within the model. GLOMAP-mode has been developed for use in the UK Met Office Unified Model (UM) as part of the new UK Chemistry and Aerosol (UKCA) sub-model. Both models use identical emissions and comparable process descriptions, although the implementation is changed where necessary. More details about the configuration used for these simulations can be found in Frontoso et al., 2008.

The calculation of aerosol optical depth is performed offline using the mass, number and relative humidity fields output from GLOMAP model. The implementation is essentially the same for both the modal and the sectional model. A Mie lookup table is used to determine the Mie extinction efficiency based upon the aerosol wet size and the complex index. In the baseline model the water uptake scheme is based upon a modified Kohler equation that allows species to be characterized by a single parameter. The
mean values of the hygroscopic parameter for ammonium sulphate, sodium chloride and organic aerosol for subsaturated air masses are 0.53, 1.12 and 0.07, respectively (Petters and Kreidenweiss, 2007). Black carbon is considered entirely hydrophobic.

PRELIMINARY RESULTS

The calculation of optical depth in GLOMAP has been evaluated against AERONET observations during the intensive LONGREX and IMPACT field campaigns (May 2008). The Aerosol Robotic Network (AERONET) is a global distribution of automated sunphotometers. Over 30 sunphotometers were operational during May 2008 over the European domain. The aerosol optical depth is calculated from the total optical depth by subtracting the Rayleigh and ozone optical depths (Holben et al., 1988). AERONET AOD is often used as a benchmark for evaluation of aerosol optical properties produced by models and retrieved from remote sensing platforms.

Fig. 1 shows the time series of AOD at 870 nm from GLOMAP-mode and AERONET sunphotometer data. The differences between AOD from GLOMAP-bin and GLOMAP-mode (not shown in Fig. 1) are about 0.01, while the differences between the model and the observations are about 0.04 and the modelled AOD is systematically less than AERONET. One reason for this difference is certainly the absence of nitrate and dust in these simulations, which causes lower values for AOD. A bigger difference (0.15) is observed on May 15. More investigations (such as looking at the aerosol size distributions) are required to understand the differences. However, the preliminary results show that the model is capable of capturing the general enhancement of AOD around mid May.

Figure 1. Time series of AOD at 870 nm from GLOMAP (red) and from AERONET (blue) over Cabauw during May 2008

Fig. 2 shows the scatter plot between AOD from sunphotometer and from GLOMAP at four European AERONET stations (Barcelona, Cabauw, Hyytiala, Leipzig and Munich) at 870 nm (on the left) and on
440 nm (on the right). With the present configuration (no dust and nitrate) the model underestimates AOD against the local sunphotometer observations at all the stations.

![Figure 2. Scatter plot between AOD from sunphotometer and from GLOMAP at four European AERONET stations (Barcelona, Cabauw, Hyytiala, Leipzig and Munich) at 870 nm (on the left) and on 440 nm (on the right).](image)

Fig. 3 shows the European distribution of AOD at 440 nm from GLOMAP-bin (on the left) and GLOMAP-mode (on the right) for May 14. There is a rather good agreement between the two models. AOD in GLOMAP-mode is slightly higher compared to AOD in GLOMAP-bin. Differences are about 0.01. However, the model is quite able to capture the general AOD pattern during that day as it is shown from the MERIS satellite data in Fig. 4.

![Figure 3. European distribution of AOD at 440 nm from GLOMAP-bin (on the left) and GLOMAP-mode (on the right) on the 14th May.](image)
They both underestimate AOD against observations. This is probably due to the absence of the nitrate and dust in the simulations. Another potential issue revealed by the satellite data is the strong spatial gradient in AOD.

**SUMMARY & CONCLUSIONS**

This work presents a preliminary analysis of the aerosol distribution over Europe during the intensive EUCAARI and LONGREX field campaigns.

The main results can be summarized as follows:

- With the present model configuration, the model underestimates the aerosol optical depth from the European sunphotometer network. Introduction of species such as nitrate and dust are required in the future simulations.
- The model is able to reproduce the general AOD pattern over Europe on May 14 compared with the satellite data.
- Quantitative comparison with satellite data is required. This is crucial in order to assess if local measurements by sunphotometer are representative of the general aerosol present around the site of measurements.

**ACKNOWLEDGMENTS**

This work is supported by the European Commission under the EUCAARI project and by the Natural Environment Research Council ADIENT project.

The authors would thank all groups and the Institutions inside LONGREX and IMPACT campaigns for providing data. The authors would also thank the PIs of the European AERONET stations for their effort in establishing and maintaining these sites.
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PRELIMINARY RESULTS OF EUCAARI FIELD CAMPAIGN IN BRAZIL

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Keywords: atmospheric aerosol, Brazil field campaign, elemental carbon, organic carbon.

INTRODUCTION

To investigate the effects of aerosols on climate and air quality we need to characterize chemical composition and physical properties of particulate air pollutants. Although several studies were performed to investigate pollutants properties in most populated regions, such as North America and Europe, we urge a better knowledge of atmospheric aerosols outside the boundaries of these traditional regions of interest. In particular, developing countries are facing a rapid growth towards industrialization and urbanization that will lead, in the closest future, to environmental issues harmful to climate and human health.

The characterization of atmospheric aerosol in developing countries is one of the objectives of the EUCAARI project, and derives from the scarcity of continuous measurements in these regions. This work reports the results of chemical characterization of fine and coarse aerosols in Manaus (Brazil), during the wet season.

METHODS AND RESULTS

Sampling site was located north of Manaus, in Central Amazonia. Here we present results from the analysis of fine and coarse aerosol samples, integrated over 72 hours, and collected continuously from February to June 2008. The climate in Central Amazonia is characterized by a wet period from January to June and a dry period from July to December [Pauliquevis et al., 2007].

Aerosol masses were obtained from gravimetric analysis (relative humidity 20%). Water soluble ion concentrations (chloride, sulfate, nitrate, ammonium, sodium, calcium, potassium, and magnesium) were measured by ion chromatography. Elemental carbon (EC) and organic carbon (OC) were characterized using an EC/OC thermo-optical analyzer (Sunset Laboratory) [Birch and Cary, 1996]. Equivalent black carbon (EBC) was measured with a Smoke Stain Reflectometer (Diffusion System) [Andreae et al., 1984] that quantifies EBC deposited on filters from the reflectance of broad-band visible light.

Figure 1 reports the average ion concentrations of fine and coarse aerosols, together with EC and OC. The higher concentration of sodium and chloride in the coarse mode was likely due to marine sources. The higher concentration of sulfate in the fine fraction indicates gas-phase condensation processes. Compared to a previous study in a nearby site [Graham et al., 2003] performed in summer 2001, OC concentration was two times larger in spring 2008; EC was larger in spring 2008, both in the fine and in the coarse mode.

The high concentration of OC observed during the present study was likely due to biogenic aerosol. The biogenic nature of OC is confirmed by the analysis of thermograms obtained from the EC/OC thermo-optical analysis. Both fine and coarse organic aerosols were characterized by a large contribution of the fraction that evolves at 450°C, which is also the dominant fraction of fulvic acid, an indicator of biogenic aerosols [Gao et al., 2006].
On average, the low EC concentration observed excludes the contribution of combustion processes to the wet season aerosols. The comparison between EC from thermo-optical analysis and EBC from reflectance measurements on filters showed a good agreement (figure 2). The presence of light absorbing aerosol different than soot might lead to an overestimation of EBC. In Manaus the difference between EC and EBC was within the error bars of EC measurements, suggesting that black carbon was the dominant light absorbing aerosol species during the sampling period.

Figure 2. Comparison of EC (thermo-optical measurements) and EBC (reflectance measurements).

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EVALUATION TOOLS FOR BLACK CARBON MODELING

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Keywords: black carbon, model evaluation.

INTRODUCTION

Black carbon is the aerosol component associated to combustion processes that plays a major role in absorbing incoming solar radiation. The ability to model black carbon is of crucial importance to determine aerosol radiative forcing [Bond and Bergstrom, 2006; Schulz et al., 2006].

Model performance is usually evaluated comparing mean of model output to mean of experimental measurements. For black carbon the mean comparison is not an accurate method to evaluate model performance, in fact model and experimental values are not normally distributed around their means.

The objective of this work is to investigate different evaluation tools for black carbon modeling.

RESULTS

Black carbon concentrations were simulated with the chemical transport model TM5 [Krol et al., 2005] coupled with the microphysical aerosol model M7 [Vignati et al., 2004]. The TM5 model is an off-line global transport chemistry model that uses the ECMWF ERA40 reanalysis data. TM5/M7 had a global resolution of 6° x 4°, and a finer resolution of 1° x 1° over Europe.

Light absorption measurements were obtained from the Global Atmosphere Watch programme (http://wdca.jrc.it/). Light absorption coefficients from aethalometer and particle soot absorption photometer (PSAP) were converted into black carbon concentrations according to specific absorption cross sections suggested by the instrument manufacturers.

Model performance was evaluated at one remote location (Point Barrow-Alaska), and four regional background sites (Mace Head – Ireland, Jungfraujoch – Switzerland, Ispra – Italy, and Bondville – Illinois) using data from July 2002 to June 2003.

Per each month, probability frequency distribution curves of 1-hour resolution data were compared; the agreement between model and experiment was quantified as the overlapping area of the frequency curves. Figure 1 reports the model/experiment agreement per each month, from July 2002 to June 2003, at Jungfraujoch. The method of the frequency curves was compared to t-student test and rank test methods [George W. Snedecor, 1989], showing an overestimation of agreement from the t-test and a dramatic underestimation of the agreement from the rank test, when the size of model dataset end experimental dataset were different.

The agreement between experiment and model was evaluated on the same datasets, varying the time resolution of data. We expected a larger model/experiment agreement from longer time resolution data, due to a smaller contribution of high-frequency noise. In a few cases, the model/experiment agreement of hourly data was larger than the agreement of daily average data: the high variability of high time resolution dataset may lead to an overestimation of model performances.
Figure 1. Model/experiment agreement from the analysis of hourly resolved data at Jungfraujoch, from July 2002 to June 2003.

ACKNOWLEDGEMENTS

We acknowledge the World Data Centre for Aerosol (WDCA: ftp://ftp-ccu.jrc.it/pub/WDCA/NARSTO_archive/2.301/parameters/Chemistry) for the access to their data archives. Dr. John Ogren (NOAA, Colorado) and Prof. Urs Baltensberger (PSI, Switzerland) are acknowledged for making their data available.

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AIRBORNE OBSERVATIONS OF AEROSOL AND CLOUD PROPERTIES DURING EUCAARI INTENSIVE CAMPAIGN WITH THE F-ATR-42

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Keywords: aerosol, cloud, microphysics, airborne measurement

INTRODUCTION

To reduce the uncertainty of the impact of aerosol particles on the climate, the European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) intensive integrated multiple aircraft and ground stations to quantify the sources and sinks of regional aerosol and their physical and chemical transformations with respect to their cloud-forming potential.

In terms of experimental infrastructures, instrumented aircraft constitute the link between local scale point measurements at ground sites and continuous satellite global observations. Compared to trace gases, aerosols show much larger variability in both vertical and horizontal scales, but often are homogeneously distributed horizontally, up to the pixel scale. Clouds are, however, very heterogeneous at the sub-pixel scale, and their microphysical and radiative properties are substantially impacted by these heterogeneities. The aircraft in-situ observations represent often the only source of data, which can help us to better document the processes controlling cloud evolution and properties. Commonly, information from satellites about the various atmospheric properties, trace gas concentrations, aerosol properties are derived products and therefore they need extensive validation against in-situ observations and here airborne measurements represents key source of such data. Furthermore, especially in case of aerosols and clouds, satellites cannot retrieve all the required properties of particles and cloud elements to assess detailed processes governing aerosol and cloud properties.

We consider here the preliminary results obtained from the in-situ airborne observations carried out with the French ATR-42 research aircraft during EUCAARI-IMPACT (Intensive Observation Period at Cabauw Tower) and LONGREX (Long Range Experiment) in May 2008.

METHODS AND PRELIMINARY RESULTS

The deployment of instruments, and their modes of operation, to measure aerosol particle and cloud droplet properties during the EUCAARI intensive campaign will be presented in this paper. The suite of instrumentation in the ATR-42 includes aerosol and CCN concentrations (CPC, CCNC), size distributions (DMA, OPC, PCASP) and optical properties (PSAP, Nephelometer), size resolved-chemical composition (AMS), lidar and radar, and cloud microphysics (FSSP, PVM, OAP). All measurements aboard were made behind an isokinetic inlet (CAI) for aerosol particles and a CVI for cloud droplets Twenty scientific flights were operated in both clear sky and cloudy conditions over the North Sea and the continental region around Cabauw (The Netherlands).

The preliminary results obtained during this experimental campaign show that during clear sky aerosol flights (May 5 to 11) aerosol sources were from east continental Europe and the polluted boundary layer
was well mixed as shown by ATR profiles (Figure 1). These flights can be considered as a contribution to the LONGREX experiment. During the cloud flights (May 13 to 30) contributing to the IMPACT experiment, all the clouds sampled were warm clouds. Most of these flights showed nucleation events (Figure 2) and different CCN compositions according to the sampling made with the CVI inside clouds. Further analysis of volatility measurements, size-resolved chemistry, dynamics and microphysics during this period will provide additional insight to the role of chemical and physical properties of aerosols on CCN activity.

Figure 1. Aerosol profile of CN, CCN (at 0.2%SS) and scattering coefficients (at 450, 550 and 700 nm) (left) and composition (right) during a clear sky flight (May 5).

Figure 2. Aerosol size distribution (dN/dlogD) during the cloud flights of May 18 showing nucleation events
THE ROLE OF RELATIVE HUMIDITY IN NEW PARTICLE FORMATION

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Keywords: Nucleation, Relative Humidity, Sulphuric acid concentrations

INTRODUCTION

New particle formation from supersaturated vapours (nucleation) can occur almost everywhere in the atmosphere, in clean, rural, coastal and polluted areas (Kulmala et al., 2004). Many recent studies of particle formation at different atmospheric environments have pinpointed solar radiation as the main key variable behind nucleation events while other factors, such as lower temperature, lower condensation sink and lower relative humidity have also been shown to favour the occurrence of new particle formation. (Boy and Kulmala, 2002; Hyvönen at al., 2005; Mikkonen et al, 2006; Hamed et al., 2007; Laaksonen et al., 2008). However not all studies of new particle formation agree on the importance of all these factors. Regarding the role of low relative humidities often observed on new particle formation (NPF) days, several explanations have been suggested. These include enhanced coagulation scavenging of sub 3-nm clusters at high RH, interference of water vapour with gas-phase chemistry producing condensable organics, diminished solar radiation at high RH leading to diminished gas-phase oxidation chemistry, and increased condensation sink (CS) of condensable gases due to hygroscopic growth of pre-existing particles. In this paper, we examine these possibilities in detail, for two different environments: San Pietro Capofiume (SPC) in the Po Valley, a highly polluted rural area and Hyytiälä station in Finland, a clean forest area. We propose that high RH’s efficiently limit gas-phase H2SO4 concentrations to low values, and that this is the main reason for suppressed NPF in humid conditions.

RESULTS AND DISCUSSIONS

In this section we present data analysis from two sites with very different characteristics regarding nucleation events and their occurrence. Hyytiälä, Finland, is a background Boreal forest site, where the air is usually rather clean, nucleation and growth rates are moderate, and the maximum frequency of event days is in the spring. San Pietro Capofiume (SPC), on the other hand, represents a polluted environment with high nucleation and growth rates, and has event frequency maximum in the summer. We use multi-year statistics from each site, to define “typical” and “extreme” events from the viewpoint of RH enhancement of condensation and coagulation sinks and subsequent effects on observed new particle formation. We then focus on the 2003 QUEST spring campaign data from Hyytiälä, because gas-phase sulphuric acid was measured during the campaign, and we are able to examine the effects of RH on H2SO4 concentrations and on nucleation rates.

Dal Maso et al. (2005) examined an eight-year dataset of nucleation events in Hyytiälä. They found that the average GR and CS during the events were 3 nm/h, and 2.4x10^-3 s^-1, respectively. We use these values to calculate the “average” RH enhancement of small particle scavenging in Hyytiälä. To define an “extreme” case, we use a growth rate from the low end of observed values, 0.5 nm/h, and a CS from the high end of observed values, 8 h^-1. It should be noted, that this pair of variables represents very extreme conditions, and we in fact do not know if it is possible at all to observe such values simultaneously during
a nucleation event. For SPC, we have a 5-year data set, from which we can determine similar average and extreme GR and CS values as for Hyytiälä. Thus, the “average” SPC case is GR = 7 nmh⁻¹, CS = 3.5 h⁻¹, and the “extreme” case is GR = 3 nmh⁻¹, CS = 75 h⁻¹ (Hamed et al., 2007).

First, we investigate the role of increased CS at high RH values on the formation rate of 3 nm particles (J₃) due to increased coagulation scavenging. Figure 1 shows how J₃ decreases as a function of RH at the “extreme” and “average” conditions. In the “average” cases, both in Hyytiälä and in SPC, J₃ drops by less than one half from its value at 10% RH. Thus, it is quite improbable that high RH values could “hide” nucleation events very efficiently at typical GR and CS values in either place. At the “extreme” conditions, on the other hand, J₃ drops by factors of 50 in SPC and as much as 50 000 in Hyytiälä. The latter number in particular indicates that nucleation event “hiding” could be taking place to some extent. The question now is, how often such “extreme” conditions occur, if at all. Figure 2 reveals that already the dry coagulation sink is large enough in the “extreme” Hyytiälä case to cause hiding of the event as J₃ is by a factor of more than 10⁶ smaller than J₁. Also, in the “extreme” SPC case, the drop from J₁ to J₃ at dry conditions is much more than the extra drop caused by increased RH. Thus, it appears that increased coagulation sink is at most a secondary reason for the observed suppression of nucleation events at high RH values.

![Graph](image-url)

Figure 1. Normalized J₃ (J₃ divided by J₃ at 10% RH) as a function or RH for the “Extreme” and “average” conditions in Hyytiälä and SPC.
Figure 2. Normalized J3/J1 as a function or RH for the “Extreme” and “average” conditions in Hyytiälä and SPC

Figure 3 shows the observed decrease of solar radiation at high RH during the 2003 campaign. Both RH and solar irradiation show a clear diurnal cycle: in the morning, as sunlight warms the ground layer, RH often starts to decrease, and will increase again when sunset approaches and air begins to cool. Hence, there is an anti-correlation between RH and solar irradiation. At an annual level this anti-correlation may be smeared, as the daily peak intensity of the irradiation varies strongly from midwinter to midsummer, but at a monthly level it should be detectable. In addition, solar irradiation can be attenuated at high relative humidity, both due to increased cloudiness, and due to enhanced scattering of sunlight by hygroscopicity grown particles (haze). This causes the production of OH radicals to decrease, and thus the production term of H$_2$SO$_4$ decreases (the same is valid of course for the production terms of condensable organics species).

It can be readily seen from Fig. 3 that the highest radiation values are limited to about 60% RH and below, and that at higher humidities the maximum values decrease as a function of RH quite steeply, especially above 90% RH. It is thus evident that high RH’s limit the production of H$_2$SO$_4$ and other condensable gases, as is also seen in Figure 4.

Figure 4 shows that the maximum H$_2$SO$_4$ concentrations decrease by more than an order of magnitude between 60-90% RH. This strongly suggests that the main reason for the suppression of nucleation at humid conditions is due to the effects by which high RH tends to decrease the source term and increase the sink term of H$_2$SO$_4$. Very likely high RH poses similar influences on condensable organics. However, it depends on the role of the organics in NPF whether RH’s suppressing action on NPF is mediated also via them. If the organics participate only in particle growth, then there is only relatively minor influence on J3 (at higher GR, the probability of a cluster to survive to 3 nm increases). However, if they participate in the actual nucleation, increasing J1, then there should be a similar influence as via H$_2$SO$_4$.

Further data analysis and model simulations are ongoing and will be presented later in future work.

112
Figure 3. RH% versus solar irradiation (Wm$^{-2}$) observed during spring 2003 QUEST field campaign in Hyytiälä, Finland.

Figure 4. RH% versus H$_2$SO$_4$ concentrations (1/cm$^3$) observed during spring 2003 QUEST field campaign in Hyytiälä, Finland.

ACKNOWLEDGMENTS.

This study is funded by Magnus Ehrnrooth foundation. ACCENT, and Academy of Finland (107826).
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SENSITIVITY OF CLOUD DROPLET NUMBER CONCENTRATION IN A GCM TO THE REPRESENTATION OF SUBGRID-SCALE VERTICAL VELOCITY

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Keywords: droplet activation, atmospheric aerosols, subgrid variability

INTRODUCTION

The activation of aerosol particles to cloud droplets depends on the supersaturation, which in turn increases with the vertical velocity $w$ of the air parcel. Therefore droplet activation parameterizations in global climate models often include a strong dependency on $w$. However, the turbulent motion in clouds is not represented in the models, and $w$ itself has to be parameterized as a function of other variables. Two different approaches have been followed in the literature: (a) assuming a probability distribution function for $w$ around its grid-mean value (Ghan et al., 1997; Storelvmo et al., 2006), or (b) enhancing or replacing the (small) grid-mean vertical velocity by an upward velocity which depends on the turbulent diffusion coefficient or turbulent kinetic energy (Lohmann et al., 2007; Morrison and Gettelman, 2008). Here we analyze the sensitivity of the simulated cloud droplet concentration in the CAM (Community Atmosphere Model)-Oslo GCM to these different assumptions on the vertical velocity.

OFFLINE SENSITIVITY STUDY

The cloud droplet activation scheme implemented in CAM-Oslo (Abdul-Razzak and Ghan, 2000) calculates the maximum supersaturation and the number of activated aerosol particles based on an equilibrium approach. The scheme takes into account the composition and size distribution of aerosol particles in up to 12 lognormal modes. The vertical velocity can be given as a gaussian probability distribution function or as a uniform updraft velocity.

Fig. 1 illustrates the sensitivity of activation to the mean vertical velocity $\bar{w}$ and the standard deviation of the vertical velocity, $\sigma_{w_{\bar{w}}}$.

Fig. 1: Activated particle fraction for different combinations of $\bar{w}$ and $\sigma_{w_{\bar{w}}}$.

The input aerosol is the same for all cases, with a total
number concentration of 1000 cm\(^{-3}\), lognormally distributed with \(\sigma = 1.5\), \(r_{g3} = 50\text{nm}\) (mass median diameter), composed of 50% sulfate and 50% organic carbon.

At \(\sigma_w = 0\) (uniform updraft), the activated fraction depends strongest on \(\bar{\omega}\). For increasing \(\sigma_w\), the curves for different \(\bar{\omega}\) approach each other. This is because while for small \(\bar{\omega}\) the broadening of the vertical velocity distribution has the effect of including higher activation from the upper tail of the distribution, the effect can be negative for high mean vertical velocities for which the broadening results in a larger part of negative vertical velocities, for which no activation is calculated. This can be most clearly seen for the case of \(\bar{\omega} = 100\text{cm/s}\), which is a very strong updraft.

It is also obvious from this figure that increasing \(\sigma_w\) for a small \(\bar{\omega}\) does not result in an as efficient increase of the activated fraction as an increase of \(\bar{\omega}\) itself by a similar amount. This is also because for small \(\bar{\omega}\) nearly half of the probability distribution function is on the negative side.

**TESTING THE TWO APPROACHES IN CAM-OSLO**

Two different approaches have been tested with the coupled aerosol-cloud microphysics scheme of CAM-Oslo. The activation scheme itself and the cloud scheme are the same for both tests, only the assumption on the vertical velocity is changed. First, as in previous versions of CAM-Oslo, a gaussian probability distribution function centered around the grid-mean vertical velocity is used. \(\sigma_w\) is then related to turbulence via the vertical turbulent diffusion coefficient \(K\) (Storelvmo et al., 2006):

\[
\sigma_w = \text{Max} \left( 30\text{cm/s}, \frac{\sqrt{2\pi K}}{\Delta z} \right)
\]

\(\Delta z\) is the layer thickness. The imposed minimum value of 30 cm/s occurs very often. Fig. 2 (left plot) shows the frequency of occurrence of different values of \(\bar{\omega}\) in cloudy gridboxes. \(\bar{\omega}\) is usually between -1 and +1 cm/s.

Figure 2: Frequency of occurrence of the grid-mean vertical velocity (left) and of the turbulent vertical velocity after (Morrison and Gettelman, 2008) (right), sampled conditionally from all cloudy gridboxes in the troposphere.

As a second approach, we have chosen the approach by Morrison and Gettelman (2008) who replace \(\bar{\omega}\) by a turbulent vertical velocity \(w_{turb}\).

\[
w_{turb} = \text{Max} \left( 10\text{cm/s}, \frac{K}{l_c} \right)
\]
In this approach a constant mixing length $l_c$ of 30 m is used. The updraft is assumed to be uniform ($\sigma_w = 0$), and always positive (upward) with a minimum value of 10 cm/s. In the right part of Fig. 2 the frequency of occurrence of different values of $w_{\text{turb}}$ is shown. Values between 10 and 20 cm/s are most frequent, but values above 100 cm/s can also occur. The high values are more frequent over land than over ocean (not shown).

For the case illustrated in Fig. 2, the two cases of $\bar{\omega} = 0$ with $\sigma_w = 30$ cm/s and a uniform updraft of 10 cm/s give very similar (and low) activated fractions. But in the case of stronger turbulence, increasing $\bar{\omega}$ is a much more efficient way of increasing the activated fraction than increasing $\sigma_w$. Fig. 3 shows the cloud-top droplet concentrations calculated with the two approaches. The probability distribution approach (left) results in totally a factor 3 less cloud droplets than the uniform updraft approach (right). Especially over ocean, the droplet concentrations in the left plot are unreasonably small, and the land-sea contrast is weak. This improves significantly with the uniform updraft approach, although large regions over ocean still exhibit concentrations below 40 cm$^{-3}$ and the global mean value is about 50% lower than suggested by satellite retrievals (not shown). The simulated cloud droplet concentrations are also very sensitive to the natural background aerosol.

![Figure 3: Droplet concentrations at the top of liquid clouds, annual mean, for the two approaches. The number given in the bottom left corner is the global mean value.](image)

CONCLUSIONS AND FUTURE WORK

The simulated droplet concentration in CAM-Oslo has been shown to be very sensitive to assumptions on the subgrid vertical velocity in clouds. So far, assuming a uniform updraft rather than a gaussian probability distribution function around the grid-mean value gives results which are in much better agreement with observations. But we know that clouds do not only consist of uniform updrafts, and in principle a distribution of vertical velocities is a more realistic representation of the subgrid-scale variability. We will pursue two approaches to improve the performance of the activation scheme with a distribution of vertical velocities: (a) a gaussian distribution which is not centered around the grid-mean vertical wind, but around a positive value related to in-cloud turbulence; and (b) non-gaussian skewed probability distribution functions as they have been observed e.g. in stratocumulus clouds.
ACKNOWLEDGMENTS

This work is supported by the Norwegian Research Council through the project NorClim and by EUCAARI. We thank Steve Ghan for providing the activation routine for the ARG scheme.

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INTRODUCTION

The particle emissions from wildfires have a large impact on both climate and air quality. Biomass burning particles are mainly internally mixed and contain a large amount of water soluble compounds, increasing the probability of activation as cloud condensation nuclei (CCN). Most of the particles are in the accumulation mode. Only the fine particles are included in this study, as the coarse particles are only few, i.e., do not have a large impact on cloud formation and also are not related to the same parameters as the fine particles.

The aim of this study is to parameterize the emissions of particle number from biomass burning, with a focus on wildfires. We have compiled and analyzed a large amount of literature data, and related particle emissions to carbon monoxide emissions as well as to the combustion efficiency and fuel.

METHODS

Most fire emissions are related to the efficiency of combustion, which can be described in different ways. The combustion efficiency, CE, is described as the part of carbon emitted as carbon dioxide, i.e. the ratio of carbon emitted as carbon dioxide divided by the total carbon emitted.

\[ CE = \frac{dC_{CO_2}}{dC_{CO_2} + dC_{CO} + dC_{VOC} + dC_{part} + ...} \]

Normally most of the carbon-containing compounds that are emitted are not measured. Thus one simplifies the description of the efficiency and uses the modified combustion efficiency, MCE, described as the ratio of carbon emitted as carbon dioxide divided by the carbon emitted as carbon dioxide and carbon monoxide. This introduces an error of only a few percent.

RESULTS

The particle size distribution changes rapidly during the first hour after emission, and is affected by many parameters. Many of the studies published count particles larger than 100 nm, for instrumental reasons. As the particle number size distributions mostly are centered only slightly above this detection limit, a large fraction of the particles are not counted, and the different lower size limits reduce the comparability. In this study both the published particle number emission, in different size ranges, and particle number emissions calculated with an assumed particle size distribution adding the particles that would be undetected below 100 nm are given and compared. The particle emissions are found to have a fairly constant ratio to the emissions of carbon monoxide of $32\pm14$ per ppb and cm$^3$ for all fuels and an assumed particle count median diameter of $\sim120$ nm, while the directly measured ratio, without corrections is $26\pm11$ per ppb and cm$^3$ (given with standard deviation and based on data from Guyon et al, 2005 and LeCanut et al, 1996). Only forest fuels has been counted with the full size distribution included and here the ratio to carbon monoxide is $28\pm12$ per ppb and cm$^3$. This data is also linearly fitted to show the relation to MCE, see Fig 1.
Figure 1. Particle number emission factors calculated from particle mass emission factors and a. similar sizes for all fuels and b. larger particles for forest fuel. The measured linear emission factor is fitted by standard methods according to Guyon et al., 2005.

Particle mass data is more abundant, and has been related to the combustion efficiency and to different fuels. As most of the particles, both as mass and number, are found in one mode, centered around ~120 nm, the data has also, quite unorthodoxly, been recalculated to particle number emissions, to compare it with the particle number emission data obtained directly, see Fig. 1a. Taking the different particle sizes from different fuels into account the calculated emission factors all are found close to the directly counted emission factor from Guyon et al., 2005, see Fig 1b. Particles emitted from forest fires are thus assumed to be 10 nm larger than average and the grass and savanna fires emitted particles are assumed to be 20 nm smaller than average (e.g. Reid et al., 2005).

CONCLUSIONS

The recommended emission factors for particle number are either related to emissions of carbon monoxide or to modified combustion efficiency. The ratio to carbon monoxide is 28±12 for forest emissions, and there is no distinguishable relation of this ratio to MCE. If the particle sizes of grass versus forest fires differ by 30 nm, as approximated from literature data (e.g. Reid et al., 2005), the emission factor for particle number is related only to MCE and not to fuel, based on the available literature data.

ACKNOWLEDGEMENTS

This work was supported by the European Commission through the EUCAARI project.

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NATURAL AND ANTHROPOGENIC CONTRIBUTIONS TO PARTICULATE MATTER IN SOUTHERN EUROPE

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Keywords: aerosols, Mediterranean, dust, sulphate, natural, anthropogenic.

INTRODUCTION

Aerosols affect atmospheric visibility, human health and climate (Seinfeld and Pandis, 1998; Kanakidou et al., 2005; IPCC, 2007). Therefore, there is a major society concern to limit their levels in the atmosphere. To achieve this goal, knowledge of the sources of atmospheric aerosol and particularly of the natural versus the anthropogenic component of them is necessary due to the human weakness in controlling the natural aerosol sources. EU drafted guidance for Member States on the natural sources contributions to particulate matter (PM_{10}, airborn particles of diameter smaller than 10 μm) and on the methods for evaluating these contributions (including modeling). Natural components of aerosol include: dust, sea-salt, biogenic nss-sulfur aerosol (sulfate, SO_2, methane sulfonic acid, MSA), natural primary organic aerosol, secondary organic aerosol (SOA) from biogenic precursors, natural nitrate aerosol (from natural nitrogen oxide, NOx, emissions).

The Mediterranean region is a cross road for air masses of distinct origin (Lelieveld et al., 2002; Mihalopoulos et al., 1997; Millan et al., 1997). Most anthropogenic sources are located to the north side of the basin and the major natural sources located inside the basin, sea-salt aerosols- and to the south of it-Sahara dust. Observations over the East Mediterranean show high concentrations of aerosols that can affect human health. The fine aerosol fraction (<1μm) is mainly composed of sulfate (35-40%), organics (30-35%), ammonium (10-15%) and black carbon (5-10%), mostly from fossil fuel and biomass combustion (Bardouki et al., 2003). High sulfate loadings in the area are mostly attributed to long range transport of pollution sources as also observed from space (Eisinger and Burrows, 1998). Only about 20% of the non-sea-salt sulfate in the area is attributed to the oxidation of dimethylsulfide of marine origin (Kouvarakis and Mihalopoulos, 2002). In addition to the particles of anthropogenic origin, significant amounts of naturally emitted airborne particles are present in the area. Large dust outbreaks from the Northern African continent are affecting the Mediterranean and to a lesser extend Central Europe. Dust reaches Europe either via vertically extended transport arriving over Crete simultaneously in the lower-free troposphere and inside the boundary layer, or via Free Troposphere Transport arriving over Crete initially into the free troposphere with the heavier particles gradually being scavenged inside the boundary layer (Kalivitis et al., 2007). Therefore, natural sources are expected to significantly contribute to the aerosol burden over Europe and particularly over the Mediterranean.

The present study applies the global 3-dimensional chemistry transport model TM4-ECPL able to simulate both the gas and aerosol phases in the troposphere (Myriokefalitakis et al., 2008) including all major aerosol components (Tsigaridis et al., 2006) in order to distinguish the contribution of various (anthropogenic and natural) aerosol components to the particulate matter over the Mediterranean. Inter-annual simulations are performed and the model results are compared with observations at selected background stations in the area.
METHODS

The 3-dimensional global chemistry transport model is a coupled aerosol and gas-phase chemistry transport model of the troposphere and lower stratosphere (Tsagaridis et al., 2005, 2006). The model has 31 vertical hybrid layers from the surface to 10 hPa and can run in two different horizontal resolutions, the low resolution of 6°x4° in longitude and latitude and the high resolution of 3°x2°. For the present study the low resolution version of the model has been used. The model’s input meteorology comes from the ECMWF operational data for 2000-2005 and is updated every 6 hours. The model is able to describe all major aerosol components together with the ozone (O₃), NOx, hydrocarbon chemistry including isoprene, terpenes and all major aerosol components, namely sea-salt, dust, sulfate, nitrate, black carbon, organic carbon, including secondary organic aerosols. The latest version of the model (TM4-ECPL) is documented in (Myriokefalitakis et al., 2008) that provides a full description of the gas phase chemistry and relevant emissions in the model whereas the aerosol modules and relevant emissions are described in (Tsagaridis et al., 2006) and references therein.

TM4-ECPL global simulations of O₃ and carbon monoxide, the major drivers of tropospheric chemistry over the Mediterranean, have been extensively and successfully evaluated by comparison with observations (Kanakidou et al., 2008 and references therein). This is giving confidence to the TM4-ECPL simulations of secondary – chemically formed – aerosol components that concern sulfur, nitrogen and organics. Systematic comparison of the aerosol simulations (Tsagaridis et al., 2006) has shown that the model simulates reasonably well the major components of tropospheric aerosol.

RESULTS

TM4-ECPL simulates the occurrence of high loadings of aerosols over Europe and particularly over the Mediterranean. Figure 1a depicts the PM₁₀ calculated by the model over Europe for August 2003 that is marked by the high dust loading close to the African coast. In the figure 1b, for comparison purposes, the PM₁₀ fraction computed when neglecting the sea-salt and dust aerosol components that are expected to dramatically affect the Mediterranean, is depicted. This aerosol mass (PM-D-SS) is composed from sulfate, nitrate and carbonaceous aerosols and maximizes over Central Europe where intensive pollution sources exist. Elevated aerosol levels are also computed over Central Balkans and the Spanish Peninsula.

![Figure 1](image)

(a) Summertime simulated surface aerosol mass PM (in µg/m³) (a) all components are considered (b) when neglecting the sea-salt and dust contributions (PM-D-SS).

The contribution of sea-salt and dust components to the total aerosol mass as simulated by the model for summertime is depicted in the figures 2, below. Dust is estimated to contribute by at least 30% to the aerosol in the extended Mediterranean area and more than 70% to the south part of the region. Sea-
salt presents important contributions both over the West (Atlantic) coast of Europe and over the Aegean Sea where this summertime contribution regionally reaches 30%.

![Figure 2. Contribution (mass ratio) to the PM mass (a) of sea-salt (SSALT/PM) and (b) of dust (DUST/PM) in the model.](image)

Multiyear surface PM$_{10}$ measurements performed in Greece (Gerasopoulos et al., 2006) and in Spain (Querol et al., 2008) but also in other EU countries (Querol et al., 2004) indicate significant contributions of dust to the PM$_{10}$ levels. In the Mediterranean, PM$_{10}$ has a similar seasonal behaviour to PM$_{2.5}$, which is marked by dust emission and transport, particularly in spring and fall in the eastern basin and in February-March and late spring-summer in the western basin (especially on regional background sites), whereas PM$_{1}$ behaves differently (e.g. Gerasopoulos et al., 2007; Querol et al., 2008). Mineral dust transport events that occur episodically over the area make a major contribution (more than 40%) to the PM$_{10}$ exceedances of the EU limit of 50 µg m$^{-3}$.

Gerasopoulos et al. (2006) found that the majority of the exceedences in PM$_{10}$ in the Mediterranean background stations are associated with mineral dust events that occur episodically over the area. Based on these observations, the EU limit of 50 µg m$^{-3}$ is exceeded at several cities. For instance this happens at Heraklion, one in 4 days, during winter and spring (50% due to transported dust) and half of the days during summer and fall (pollution). Gerasopoulos et al. (2006) have shown that pollution contributes significantly to the PM$_{10}$ levels over the area during summer. In industrial and urban areas, most exceedences (around 70-80%) are due almost exclusively to local anthropogenic sources (Querol et al., 2008).

In Figure 3, the PM$_{10}$ observations over Crete are compared with the simulations by the TM4-ECPL model. Similar comparison is shown for observations over Spain in Figure 4. These comparisons between observations (daily mean over Crete and monthly mean over Spain) and monthly mean simulated PM levels show the ability of TM4-ECPL model to reproduce the aerosol levels and their temporal variability and enables the use of the model to evaluate the contribution of the various sources to PM$_{10}$ levels in the area.

The Mediterranean atmosphere with high levels of oxidants is a photochemical reactor where interactions between natural and anthropogenic emissions enhance aerosol formation. These oxidants initiate reactions that form acids, including sulphuric and nitric acids, and secondary aerosols. The high sulfate loadings in the area are mostly attributed to the long-range transport of sulfur-dioxide pollution. Of particular interest for the sulfur abatement strategy is that during summer in the eastern Mediterranean, heterogeneous sulphate production on fine particles appears to be negligible whereas only about 10% of the supermicron nss-sulphate can be explained by condensation of gas-phase sulfuric acid; the rest must be formed via heterogeneous pathways (Mihalopoulos et al., 2007).
The ability of TM4-ECPL model to simulate the observed sulphate levels in the Mediterranean, is demonstrated in Figures 3 and 4 (middle panels) that is mostly produced from sulfur dioxide oxidation to sulfuric acid leading to sulphate in the particulate phase. The bottom panels of the figures 3 and 4 that compare the carbonaceous aerosol observations with the model results show that TM4-ECPL successfully reproduces the observed monthly mean levels and their variability at background stations of both the West and the East basins of the Mediterranean.

![Graphs showing PM10, SO4, and OC-EC concentrations over time]

Figure 3. (top) PM10 observations (open circles) at Heraklion (Crete, Greece) from Gerasopoulos et al. (2006) and comparison with the TM4-ECPL model simulated monthly mean levels (closed circles). The contribution of dust is also depicted (yellow triangles). (middle) Observations (open circles) and model simulated (solid squares) levels of sulphate aerosol (SO$_4^-$) at Finokalia, Crete about 70 km North of Heraklion. (bottom) same as middle but for carbonaceous aerosols (organic and black carbon).

CONCLUSIONS

In the Mediterranean PM10 and PM2.5 exceedence are mainly linked to dust aerosols. Mediterranean aerosol contains also significant amounts of sea-salt components. The high PM levels due to natural components – dust events over the Mediterranean can be predicted but cannot be controlled. Measures to take are limited on alert if needed (visibility, respiratory problems etc). Exceedences due to natural aerosols should not imply penalty to the concerned country.
Note however that the Mediterranean atmosphere with high levels of oxidants is a photochemical reactor where interactions between natural and anthropogenic emissions enhance aerosol formation. Natural primary organics, pollen, could be coated by pollution nitrated compounds. Dust aerosols could be associated with living organism. Natural emissions of organics have been shown to increase the anthropogenic component of aerosols as is the case of the dimethyl sulhide that is naturally emitted from the oceans and through reaction with nitrate radical of anthropogenic origin is forming nitrate particles thus contributing to nutrient deposition to the sea (Vrekoussis et al., 2006).

It remains a topic of debate how to separate the natural from the anthropogenic component in PM levels on routine basis. PM1 could help monitor pollution since it is shown to behave differently than dust. Organic to elemental carbon measurements, satellite observations, sunphotometer observations, air mass trajectory calculations can also help identifying events. Dust and sea-salt can be now forecasted although with significant uncertainty, whereas organic aerosol require better representation in models. Further work is needed to properly simulate organic aerosol in particular since this aerosol component is expected to gain importance in the future (Tsigaridis and Kanakidou, 2007).

Acknowledgements. Part of this work has been performed within the EU funded project EUCAARI. SM acknowledges support by PENED-373 grant.
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SULFATE AEROSOL NUCLEATION, PRIMARY EMISSIONS, AND CLOUD RADIATIVE FORCING IN THE AEROSOL-CLIMATE MODEL ECHAM5-HAM

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Keywords: nucleation, cloud condensation nuclei

INTRODUCTION

Aerosol nucleation from the gas phase is a major source of aerosol particles in the Earth’s atmosphere, contributing to the number of cloud condensation nuclei and consequently of cloud droplets. Nucleation can therefore act upon cloud radiative properties, cloud lifetimes, and precipitation rates via the first and second indirect aerosol effect. However, freshly nucleated particles measure a few nanometers in diameter, and need to grow to sizes of tens of nanometers in order to participate in atmospherically relevant processes. Depending on the availability of condensable molecules, this process may proceed on time scales between minutes to days. Concurrently, the aerosol particles that formed from the gas phase compete with aerosol particles emitted from the surface for condensable material. Therefore, cloud radiative properties, cloud lifetimes, and precipitation rates will depend to various degrees on aerosol nucleation rates and on the individual nucleation pathways. Here we discuss the role of new particle formation from the gas phase for cloud radiative properties and the contributions of the considered nucleation pathways as well as of particulate sulfate emissions.

METHODS

We have replaced the scheme describing the formation of new particles from the gas phase based on laboratory thermochemical data for neutral and charged nucleation of sulfuric acid and water into the aerosol-climate model ECHAM5-HAM (Stier et al., 2005) following an approach by Kazil and Lovejoy (2007). Concurrently, a new method for the integration of the time evolution equation for the concentration of gas phase sulfuric acid has been implemented in the M7 aerosol microphysics module (Vignati et al., 2004) of ECHAM5-HAM.
RESULTS

Our simulations (see Fig. 1) show that sulfate aerosol nucleation plays an important role for cloud radiative forcing, in particular over the oceans and in the southern hemisphere. A comparison of the simulated cloud radiative forcing with satellite observations shows the best agreement when both neutral and charged nucleation proceed, with neutral nucleation playing a minor role in the current model version. In contrast, switching off nucleation leads to a systematic bias of the results away from the observations, indicating an important role of aerosol nucleation in the climate system. Discrepancies of results and observations, in particular in the northern hemisphere may be possibly explained with unaccounted nucleation mechanisms, such as ternary and organic nucleation.

REFERENCES


CCN climatologies

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Abstract. Recent studies have shown that for the purpose of assessing CCN activity, the influence of aerosol composition can be efficiently represented by a single parameter such as the effective hygroscopicity parameter $\kappa$. Knowledge of this parameter (continental $\kappa = 0.3 \pm 0.1$ and marine $\kappa = 0.7 \pm 0.2$) combined with knowledge of concentration and size for ambient aerosol enables efficient calculations of CCN concentration as function of water vapor super-saturation. Thus, in conjunction with newly derived aerosol climatology for aerosol properties, which define aerosol concentration and microphysics, global monthly maps for concentrations of cloud condensation nuclei (CCN) are given and also estimates for CCN enhancements due to anthropogenic activity are provided.

Key Words: tropospheric aerosols, aerosol cloud interaction, anthropogenic impact

INTRODUCTION

Aerosols can act as cloud condensation nuclei (CCN). Thus, aerosol can modify cloud microphysics with potential impacts to the macrophysics of clouds (e.g. cloud structure, frequency or lifetime) and to the hydrological cycle (e.g. precipitation intensity, frequency or distribution). Thus, there is a need to quantify the number of available aerosol particles that can serve as nuclei. And in the context of a changing climate, there is particular interest in anthropogenic-enhanced CCN amounts. Necessary ingredients for CCN estimates are information on highly variable aerosol properties in space and time. Here, amount, size and composition are derived from a newly developed climatology for aerosol optical properties in conjunction with a new concept, which simplifies aspects of aerosol humidification. First maps of the new aerosol climatology are presented. Then the new concept for characteristic humidifications by continental or marine aerosol mixtures is introduced. And finally all aerosol information is combined to yield global monthly CCN maps as function of super-saturation. And with support from global modeling even estimates for anthropogenic CCN enhancements are offered.

NEW AEROSOL CLIMATOLOGY

The new climatology for aerosol optical properties is defined by monthly maps for (mid-visible) aerosol properties of aerosol optical depth (AOD), single scattering albedo ($\omega_0$) and Ångstrom parameter (AnP). The climatology is tied to quality data by ground-based monitoring, which is spatially and temporarily extended and for complete coverage with median data by global modeling (Kinne et al., 2006). Monthly maps for AOD, $\omega_0$ and AnP are presented in Figure 1, Figure 2 and Figure 3, respectively.
Figure 1. monthly global maps for the mid-visible aerosol optical depth of the new climatology

Figure 2. monthly global maps for the mid-visible single scatt. albedo of the new climatology
Figure 3. monthly global maps for the mid-visible Ångstrom parameter of the new climatology

AOD data in Figure 1 indicate aerosol amount, $\omega_0$ in Figure 2 illustrate with deductions from 1.0 usually regions with increased aerosol absorption potential (e.g. biomass burning in Southern Africa) but very large dust sizes (e.g. over the Sahara) and AnP in Figure 3 indicates, where aerosol particles are predominantly larger (having a smaller AnP, e.g. in regions with dust-outflow or sea-salt) or where aerosol particles are usually smaller (having a larger AnP, e.g. regions with urban pollution or biomass burning).

NEW CONCEPT ON AEROSOL HUMIDIFICATION

Aerosol properties are always mixtures of many components and so that the relevant properties (e.g. dissociation constants, activity coefficients) which determine water uptake are not well known. Therefore, two classes of empirical techniques have been developed to characterize the hygroscopicity of ambient aerosol, either extrapolate measurements of the water uptake and hygroscopic growth from sub-saturated conditions (e.g. hygroscopicity tandem differential mobility analyzers [HTDMA]) or directly measure the activation of CCN with counters [CCNC] in the super-saturated conditions (e.g. thermal gradient diffusion chambers and flow tubes). Rather than dealing directly with measurements an effective hygroscopicity parameter $\kappa$ has been proposed (Petters and Kreidenweis(2007) that relates the volume of water uptake by aerosol to the activity of water in the formed aqueous droplet. Values of $\kappa$ with the Formula 1 below enable efficient calculations of values for critical super-saturation $S_c$ or critical dry particle diameter $D_S$ according to Köhler theory (Rose et al., 2008).
Here the Raoult effect (soluble components in reducing water activity) is described by $\kappa$, and the Kelvin effect (the equilibrium vapor pressure over such a strongly curved surface is much greater than that over a flat surface) is described by the parameter $A$ as a function of the solution surface tension ($\sigma_s$), temperature ($T$), ideal gas constant ($R$), density ($\rho_w$) and molar mass of water ($M_w$): 

$$A = \frac{4\sigma_s M_w}{RT\rho_w} \approx 0.6 \times 10^6 \text{Km} / T.$$ 

Assuming additivity for water activity of multi-component solutions, the effective $\kappa$ can be expressed by linear combinations of $\kappa_j$ of its individual chemical components, weighted by their volume fraction. Characteristic $\kappa_j$ are in the range of $\sim 1.3$ for NaCl, $\sim 0.6$ for (NH$_4$)$_2$SO$_4$, $\sim 0.2$ for levoglucosan and various organic acids, and $\sim 0.1$ for secondary organic aerosols (SOA). $\kappa$ values for biomass-burning particles range from about 0.01 for very fresh smoke containing mostly soot particles to 0.55 for aerosols from grass burning. The available data suggest that after short aging on a time scale of hours, most pyrogenic aerosols will have $\kappa$ values in the range of 0.1 to 0.3 (Petters and Kreidenweis, 2007; Andreae and Rosenfeld, 2008). A summary of $\kappa$ values derived from various sources is presented in Figure 4.

**Figure 4.** Average relations between critical super-saturation and aerosol dry diameter (Andreae and Rosenfeld, 2008). The colored bands reflect polluted continental and clean marine data from Hudson (2007), the colored dots with colored borders are from Dusek et al. (2006) and Andreae and Rosenfeld (2008). The colored dots with grey borders have been recalculated from Kandler und Schütz (2007). The lines representing constant effective hygroscopicity parameters $\kappa$ are from Petters and Kreidenweis (2007).
The data plotted in Figure 4 show that continental aerosols fall in a narrow range of κ values around 0.3 (Dusek et al. 2006, Hudson 2007) which suggests that aerosol humidification of continental aerosol is almost invariant to aerosol composition and that CCN activity is mainly controlled by aerosol size. The plotted data for clean marine data indicate higher values, from around 0.6 (Allan et al., 2007) to around 0.9 (Hudson, 2007, Kandler and Schütz, 2007). Thus, κ values of 0.3 over oceanic regions and of 0.7 over continental regions were assumed in subsequent CCN simulations.

**CCN CONCENTRATIONS**

Aerosol particles, acting as CCN, allow atmospheric water vapor to condense and form cloud droplets. This condensation occurs preferably on larger aerosol sizes, because lower super-saturations are required to overcome their surface curvature tension. Thus, only the larger aerosol sizes are of interest (here, as well as for radiative transfer impacts). Potential CCN are all aerosol particles of the coarse size mode (radii larger than 0.5µm) and the larger sizes of the accumulation size mode (0.05 to 0.5µm radius). The critical aerosol size, above which aerosols can serve as CCN, is (in the context of a well defined hygroscopicity parameters κ of 0.3 over continents and of 0.7 over oceans) primarily a function of the water vapor super-saturation. Typical values for super-saturation are near 0.1% and up to 0.5% for more convective cloud systems. Applying Formula (1) places the critical radii at 80nm (over land) and 30nm (over oceans) for a super-saturation of 0.1% and at 60nm (over land) and 20nm (over oceans) for a super-saturation of 0.5%. Thus, over land as much as 50% of the pollution or biomass (accumulation size) aerosol may be too small to serve as CCN, whereas over the ocean almost all accumulation (and of course coarse) aerosol sizes can be potential CCNs.

The required information on size and (local) aerosol amount is supplied by data and concepts associated with the new aerosol climatology. Aerosol amount is based on global AOD maps of Figure 1, where sun-photometer data have been merged onto a modeling background. For the necessary vertical distribution of the AOD, monthly average data from global model simulations were applied. As part of AeroCom model evaluations (Giubert, pers. comm.), general agreement between simulated aerosol vertical distributions and lidar profiles has been demonstrated. However, given the diversity in modeling and a growing database by active remote sensing from space, it is recognized that the use of model data at this stage is a pragmatic choice, to satisfy data-needs. At a later stage, data on aerosol vertical distribution will certainly be better constrained by active remote sensing data from ground and space. Aerosol size is based on the assumption of a bi-modal, log-normal distribution, distinctively separating the coarse size mode and the accumulation size mode. Apportionment of AOD to each mode (AODₐ, AODₐ) is tied to the observed mid-visible AOD spectral dependence characterized by the AnP in Figure 3. The AOD separation is achieved by the coarse mode’s spectral insensitivity along with a prescribed spectral dependence for the accumulation mode. The coarse mode composition (either dust or sea-salt) as well as the dust size are defined by the mid-visible ø₀ in Figure 2. More specifically, the coarse mode assumes a log-normal distribution with a fixed distribution width (standard deviation 2.0). The assumed mode radii are 0.75 µm for sea-salt and 0.375 µm for dust.
It should be noted, however, that larger dust sizes are successively chosen (0.75, 1.5 or 3.0 µm), if (small) particle absorption alone is unlikely to explain locally the low \( \alpha_0 \) of the climatology. The smaller accumulation mode also assumes a log-normal size distribution with a fixed (though narrower) distribution width (standard deviation 1.7). In conjunction with the prescribed AnP (completely dry: 2.2, completely wet: 1.6) the mode radius is defined to lie between 0.085 µm under completely dry and 0.135 µm under completely wet conditions (where low cloud cover of a cloud climatology is applied to define wetness).

Three types of CCN concentrations are considered. In the first scenario all aerosols of both coarse and accumulation size modes are considered. In the second scenario supersaturations of up to 0.5% are permitted. This required that the log-normal distribution of the accumulation mode needed to be truncated from sizes smaller than 60nm over land and smaller than 20nm over oceans, as these particles were too small to be activated. In the third scenario the maximum super-saturation was set to 0.1%, with cut-off sizes at 80nm over land and 30nm over oceans. Simulated CCN concentrations at about 1km above the ocean or land surface are displayed in Figure 5 (in log10 space) separately for total, natural and anthropogenic aerosol.

![Figure 5](image-url)

**Figure 5.** Annual average global maps for CCN concentrations without cut-offs to sizes of the accumulation mode (left panels), at 0.5% super-saturation (center panels) and at 0.1% super-saturation (right panels). Concentrations are displayed (in log10 per m³) separately for total aerosols (top panels), natural aerosols (center panels) and anthropogenic aerosols (bottom panels).
CCN concentrations of Figure 5 are given for a logarithmic scale and for annual averages. Monthly CCN fields for total (natural and anthropogenic aerosol) - now in a linear scale - for 0.1% and 0.5% super-saturations are presented in the Appendix. They indicate seasonal variations (e.g. increases during the tropical biomass burning season) and demonstrate that CCN concentrations increase (on a global average basis) by about 30%, when relaxing the super-saturation from 0.1% to 0.5%. It should be noted that CCN concentrations of the accumulation mode are about one order of magnitude larger than CCN concentrations of the coarse mode. Thus, it does not surprise, that monthly maps for the CCN anthropogenic fraction which are provided in the Appendix, resemble the monthly maps for the anthropogenic fraction for AOD of Figure 6.

Figure 6. monthly maps for the anthropogenic fraction of the AOD fraction of the accumulation size mode (for aerosol size smaller than 0.5μm in radius) based on global model simulations, where model output of two specific AeroCom experiment (Schulz et al. 2006) was compared: AOD predictions applying current (year 2000) emissions and AOD predictions applying pre-industrial (year 1750) emissions for primary aerosol and precursor gases (Dentener et al. 2006). In these simulations anthropogenic aerosols (mainly sulfate and carbonaceous aerosols) only populated the smaller accumulation sizes and the anthropogenic fraction $f_{\text{A,ANT}}$ given in this Figure only refers to the AOD$_\text{A}$: $f_{\text{A,ANT}} = [\text{AOD}_{\text{A,2000}} - \text{AOD}_{\text{A,1750}}] / \text{AOD}_{\text{A,2000}}$. 
The number of CCN concentration changes with altitude. Thus, CCN concentrations were determined at two additional altitudes of 3km and 8km, for information to cloud development at higher altitudes. Simulated CCN concentrations for a 0.1% supersaturation at these three altitudes are compared in Figure 7 (in log10 space), again separately for natural, anthropogenic and total (anthropogenic and natural) aerosol.

Figure 7. annual average global maps for CCN concentrations at 0.1% super-saturation at different altitudes (1km above the ground: lower panels, at 3 km: center panels, at 8 km: top panels). Concentrations (in log10 per m$^3$) are shown for total aerosols (left panels), for natural aerosols (center panels) and for anthropogenic aerosols (right panels).

The simulated total (natural and anthropogenic) CCN concentrations are in general agreement with Glomap simulations (Spracklen et al., 2008). Their global annual average at the surface and for a 0.2% super-saturation is about twice as large as the estimate of this study for 1 km altitude and a 0.1% super-saturation. There is also agreement on the seasonal cycle as July CCN concentrations (northern hemispheric summer) are higher than for December. Most maxima match (e.g. industrial regions). The largest differences are Glomap simulated CCN sinks in the ITCZ, which are likely caused by cloud-processing in the Glomap model.

Of particular interest are CCN anthropogenic enhancement factors defined by the ratio between anthropogenic and natural concentration. Since the annual ratios resemble each other at different super-saturations and altitudes, enhancement factors are presented on a
monthly basis in Figure 8 for the most interesting and likely case: for water clouds at lower altitude and 0.1% super-saturation.

Figure 8. Monthly global maps for anthropogenic enhancement of CCN concentrations over natural CCN at 0.1% super-saturation at 1km above the ground.

The monthly maps in Figure 8 illustrate that anthropogenic enhancements occur primarily in the Northern Hemisphere, predominantly near industrial areas. Anthropogenic CCN enhancements are greater during the winter season, at which time these anthropogenic enhancements appear to have a significantly impact in the Arctic.

CONCLUSION

Monthly global maps have been developed to derive estimates for CCN and also CCN enhancement due to anthropogenic activities. These maps are linked to a new monthly climatology for aerosol optical properties, which is tied to quality measurements from ground-based monitoring networks. This application certainly demonstrates the value of well maintained and calibrated ground networks, with additional applications as test-bed to global modeling and evaluation tool for satellite data retrieval techniques. In this study many data-sources had to rely completely on modeling, because data were either unavailable or lacking in accuracy. Future efforts should explore new measurement based data-set sources to constrain the freedom in modeling or to replace simulations. A good example is upcoming information on vertical profiling from active remote sensing.
The various global maps created for this contribution relied on many assumptions and applied often rather simple methods. There is obviously room for improvement and fine-tuning. In that sense, the values indicated for (tropospheric) aerosols were intended to provide general numbers on amount, spatial distribution, and seasonality. Despite providing estimates for CCN concentrations, the cloud related aspect of aerosols remains unclear. Little is known about what happens in cloudy environments to aerosol or cloud particles due to interactions, as almost all aerosol data are associated with cloud-free conditions. New measurements (e.g., active remote sensing, high temporal resolution data) and modeling concepts (e.g., bridging modeling scales) are needed to move beyond questionable statistical associations.

Acknowledgements

The work was supported by EU-projects GEMS and EUCAARI. Efforts of many global modeling groups contributing to AeroCom exercises and the support of the AERONET group by providing input on site assessments for data quality and regional representation, is gratefully acknowledged.

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ATMOSPHERIC MOLECULAR CLUSTERS IN BOREAL FOREST

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Keywords: neutral clusters, particle formation, pulse height CPC

INTRODUCTION

Direct measurements of atmospheric molecular clusters are crucial to understand the dominating nucleation mechanism in boreal forest. Due to instrumental limitations observations of neutral clusters have been sparse. A significant effort has recently been put into developing instruments capable of measuring neutral particles below 3 nm, which is the lower detection limit of the current commercial instruments. With newly developed measurement techniques, like neutral cluster and air ion spectrometer (NAIS) and CPC-based applications, Kulmala et al. (2007) and Sipilä et al. (2008; 2009) observed a persistent pool of neutral sub-3 nm clusters in boreal forests. Here we present a continuous time series of atmospheric neutral cluster concentrations. We also study the diurnal variation of cluster concentration in boreal forest, which gives insight into their production mechanisms. By measuring simultaneously both charged and neutral clusters with various independent instruments we aim at estimating the significance of ions in producing neutral clusters.

MEASUREMENTS AND METHODS

The measurements took place at SMEAR II station (61°51′N, 24°17′E, 181 m ASL) in Hyytiälä, southern Finland during 15 March – 26 June 2007 and 1 – 31 May 2008. Neutral particles and clusters were measured with a pulse-height condensation particle counter (PH-CPC). Supportive data sets of particle and ion size distributions measured with DMPS, NAIS, BSMA and AIS were also available from the station.

Figure 1. Detection efficiency of the PH-CPC for positively charged $WO_x$-particles and charger-generated ion clusters at different saturator temperatures ($37^\circ C$ being nominal) keeping condenser temperature constant at $10^\circ C$. The solid line describes the transport efficiency from the inlet to the condenser.
The pulse height analysis technique (e.g. Saros et al., 1996) relies on detecting the intensity of light scattered by particles after their condensational growth in the CPC. Due to supersaturation gradient inside the condenser, particles activate for growth at different axial positions depending on their size. The smaller the particle, the later it will be activated leading to smaller final droplet sizes. The PH-CPC used in this study comprises a TSI-3025A ultrafine CPC with modified optics (Dick et al., 2000) and a multichannel analyzer. For increasing the detection efficiency of small particles, the supersaturation inside the condenser was increased from nominal until homogenous nucleation appeared. The pulse height analysis technique allowed us to distinguish homogenous nucleation from activation of clusters and resolve the size distribution of particles below 5 nm. As depicted in figure 1, we were thus able to detect clusters down to mobility diameter of \(~1.2\) nm with a detection efficiency of several percents. Detailed description of the performance of the instrument and data inversion is published by Sipilä et al. (2009).

RESULTS AND CONCLUSIONS

The concentration of molecular clusters smaller than 3 nm seems to be highly variable in boreal forest environment. The concentration varied typically between 500...50 000 cm\(^{-3}\), the medians being 8060 cm\(^{-3}\) in year 2007 and 3380 cm\(^{-3}\) in 2008. A time series from 2007 is presented in figure 2. The number of neutral clusters seems to considerably exceed the charged ones, as the measured cluster concentrations were usually at least one order of magnitude higher than total ion cluster concentrations. Also the contribution of ion-ion recombination products (calculated maximum estimate) to total neutral cluster concentration was found to be minor, the median being 4.9%.

![Figure 2](image_url)

Figure 2. (a) Number concentration of \(<\) 3 nm neutral clusters (black dots) and 1.5...2 nm recombination products (gray line), (b) concentration of ions 0.8...1.3 nm (black dots) and 1.3...3.2 nm (gray line). Data are calculated from PH-CPC and BSMA measurements in March – June 2007 in Hyytiala.

Since the uncertainties regarding cluster concentrations are still large, the reported concentrations should be considered as our best estimates. However, the diurnal and day-to-day variation of clusters can be studied; a distinct diurnal variation with a clear night-time maximum was indeed found (figure 3). Our results support the concept that formation of clusters and their activation for growth are two distinct...
processes as neutral clusters are readily formed in the night-time, when no particle formation is observed. Before and during most new particle formation events the cluster formation rate rose only slightly, or remained close to stable.

Figure 3. Median diurnal variation of (a) 3…5 nm particle concentration and (b) < 3 nm neutral cluster concentration in May 2008 in Hyytiälä. Days are classified into event (black line, 16 days), non-event (gray line, 2 days) and undefined (dashed line, 13 days) according to Dal Maso et al. (2005).

ACKNOWLEDGEMENTS

This work has been partially funded by European Commission 6th Framework programme project EUCAARI, contract no 036833-2 (EUCAARI). Maj and Tor Nessling foundation is acknowledged for financial support.

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A MODEL STUDY ON GROWTH RATES OF NEUTRAL AND CHARGED PARTICLES

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INTRODUCTION

The formation of new atmospheric aerosol particles and subsequent growth has been found to take place in a variety of environments (see Kulmala et al., 2004, and references therein). In order to quantify the effects resulting from atmospheric aerosol formation, we should have better understanding on the initial steps of this phenomenon. Unfortunately, the great majority of the conducted measurements are not suitable for investigating the very early steps of aerosol formation due to instrumental limitations.

Air ion spectrometers provide a means to measure the number distributions of charged particles and ion clusters down to molecular sizes (e.g. Mirme et al., 2007; Asmi et al., 2008). The drawback of most of these instruments is that they are unable to measure neutral nanometer-size particles which, are usually expected to dominate over corresponding charged particles.

METHODS

In this study we have used a newly-developed box model Ion-UHMA. The Ion-UHMA is based on the aerosol dynamical model UHMA (Korhonen et al., 2004), onto which we have added charge dynamics from the model AEROION (Laakso et al., 2002). The main dynamical processes in the model are condensation, coagulation, nucleation, ion-aerosol attachment and dry deposition. There are three particle charge classes in the Ion-UHMA: neutral, negative and positive. In addition to the growing particles there are pools of charged clusters in the model. The attachment and recombination of clusters with growing particles are simulated and the formation of new (neutral or charged) particles is assumed to act as a sink for the (neutral or charged) clusters.

A series of simulations was conducted to study the correlation between the “apparent” growth rate of the charged particles and the “real” growth rate of neutral particles. The formation rates of the particles were given as model inputs and the particles were assumed to consist of sulfuric acid, ammonia, water and single organic compound. The condensing vapors used were sulfuric acid and organic vapor. The main varied parameters were the particle formation rate, condensing vapor concentrations, initial particle size distribution and fraction of ion-induced nucleation.

Out of the simulated data, the “apparent” particle growth rates were determined by following the change in concentration maximum of the nucleation mode. A straight line was fitted to the time and diameter coordinates of the mode centre and the growth rate was obtained as the slope of the line. The mode centre was determined either by fitting a log-normal distribution at each time step or by searching the concentration maximum of each size section as a function of time. The procedure was repeated for all charge classes and results were grouped to three size ranges (1.7-3 nm, 3-7 nm and 7-20 nm).
The methods used to determine the growth rate worked reasonably well in most of the cases (Figure 1). Even when the “real” growth rates of charged particles were much higher than the “real” growth rates of neutral particles, the “apparent” growth rates of charged particles were relatively close to the “real” growth rates of neutral particles. This was due to dominance of neutral particles over corresponding charged particles and interactions between neutral and charged particles and ions. The results would lead to a conclusion that the “apparent” growth rates of the charged particles could be used to estimate the “real” growth rates of neutral particles.

Though there is variation in the relation between the “apparent” and “real” growth rate, the method used seems to somewhat underestimate the “real” growth rate on average. A set of three simulations was conducted to investigate the reason for the systematic error.

In the three simulations the particle formation started in the beginning of the simulation and was ended after one, three or five hours (cases 1, 2 and 3). The growth rate of particles was constant as a function of both time and particle diameter, and particles were set to grow after the first hour of simulation. Thus the new particle formation event was very burst like in the case one and broader in the two other cases.

In Figure 2 there is time evolution of the centers of the growing modes for the neutral modes in all three cases, charged modes of the case 1 and diameter of a neutral reference particle. The growth rates are obtained as a slope of the curves. Comparison between the neutral modes demonstrates that the ongoing particle formation slows down the evolution of the mode center and thus leads to smaller “apparent” growth rate. Also the growth rate of charged modes seems to be bigger than the growth rate of neutral mode for case 1. This is due to higher charging probability for bigger particles. When the particle mode grows to bigger sizes, the concentration of charged particles is effectively getting bigger, which moves the mode center towards bigger sizes and leads to higher growth rates. The effect is opposite for the neutral particles. Still even the charged particle modes of the burst like event (case 1) grow slower than the neutral reference particle. This is due to numerical diffusion in the model.
Figure 2 The time evolution of mode centers in three cases. The three lowermost lines mark the neutral modes in all the cases, the grey lines (on top of each other) mark the charged modes of the case 1 and the uppermost line mark the diameter of neutral reference particle.

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INTRODUCTION

Aerosol particles influence the climate both directly by interacting with the incoming radiation, and indirectly acting as seeds for the formation of cloud droplets (Twomey, 1991). The secondary aerosol formation by nucleation and subsequent growth to cloud condensation nuclei sizes of atmospheric aerosol particles has been observed at various locations around the world (Kulmala et al., 2004). Despite the growing list of locations where frequent aerosol formation has been observed, the overall magnitude of this source of aerosol is still not well understood. The detailed formation mechanisms and the chemical composition of the freshly formed particles are still largely uncertain.

The activation of existing charged and neutral clusters has been proposed as a possible candidate for aerosol formation. Many questions remain regarding the composition and the electric charge of those clusters. Which vapours are responsible for the first steps of nucleation? The main processes responsible for formation and growth of secondary particles need to be known to assess the importance of particle formation and growth on the Earth’s climate.

As part of the EUCAARI campaign (European integrated project on aerosol cloud climate air quality interactions), different types of ion spectrometers, have been operating in a total of 13 selected field sites (so-called EUCAARI sites). The different instruments are the AIS (Air Ion Spectrometer), the BSMA (Balanced scanning Mobility Analyzer), the NAIS (Neutral cluster and Air Ion Spectrometer) and the ANAIS (Airborne-NAIS). The measurements started during the EUCAARI Intensive Observation Period (IOP) in March 2008. The AIS measures mobility distributions of charged aerosol particle. The NAIS is capable of measuring mobility distributions of sub-3 nm neutral and charged aerosol particles and clusters (Kulmala et al., 2007).
METHODS

Measurement data used in this study has been collected from 13 field sites around Europe as well as from one site in South Africa. The different instruments started measuring on March 2008 and will continue until the end of May 2009. The exact starting times varied on different locations (from March to June). The database includes continuous measurements, intensive measurement periods and shorter measurement campaigns. Continuous or campaign-wise measurements have been conducted in Hyyitälä and Pallas (Finland), Vavihill (Sweden), Mace Head (Ireland), Cabauw (Netherlands), K-puszta (Hungary), Hohenpeissenberg and Melpitz (Germany), Po Valley (Italy), Jungfraujoch (Schwitzerland), Puy de Dome (France), Finokalia (Greece) and Rustenberg (South Africa). These stations can be seen from the map in Figure 1. Each one of these stations has a particular environment. For example, some of the stations are marine coastal sites, while some are continental and others rural, etc. An Airborne Neutral cluster and Air Ion Spectrometer (ANois) took part in the airborne measurements in an instrumented aircraft over the European field stations.

Figure 1. Locations of the different spectrometers (BSMA, AIS and NAIS) in the EUCAARI measurement sites.

The Air Ion Spectrometer (AIS, Mirme et al., 2007) measures simultaneously mobility distributions of both negative and positive air ions in the range from 2.39 to 0.001 cm$^2$ V$^{-1}$ s$^{-1}$, which corresponds to a mobility diameter range of 0.8-47 nm. The AIS consist of two identical cylindrical differential mobility analyzers (DMAs) equipped with insulated electrometer rings. Sampled ions are collected on the electrometer rings in 21 electrical mobility fractions for both polarities. The Neutral cluster and Air Ion Spectrometer (NAIS) is a modified version of the AIS. Controlled charging together with electrical filtering enables to measure also the neutral aerosol particles. The measurement principle of the NAIS is
based on unipolar charging of sampled particles and their subsequent detection with an electrical mobility analyzer. The mobility range of the NAIS is 2.39-0.001 cm$^2$ V$^{-1}$ s$^{-1}$, which corresponds to a mobility diameter range of 0.8-47 nm. The charger ion mobility range from 1.3 to 1.6 cm$^2$ V$^{-1}$ s$^{-1}$ represent the lowest estimation for the detection limit, which is approximately 2 nm. Particles below this limit cannot reliably be distinguished from the charger ions.

The Balanced Scanning Mobility Analyzer (BSMA, Tammet, 2006) measures mobility distributions of small air ions and naturally charged aerosol particles of both negative and positive polarity. The mobility range of the BSMA is 3.2 to 0.032 cm$^2$ V$^{-1}$ s$^{-1}$, which corresponds to a mobility diameter range of 0.8 to 7.6 nm. The BSMA consists of two plain condensers, one for each polarity, and a common electrical amplifier connected to a balanced bridge circuit. Size segregation is obtained by discharging a capacitor through the repelling electrode and monitoring the electrometer current in the balanced bridge circuit. An inlet gate lets either positive or negative ions pass through the aspiration condenser.

**RESULTS**

The measurements are still continuing non-stop until this day, apart from some data gaps due to technical difficulties. Some changes have also occurred in some stations. For example, the measurements were started with an NAIS in Cabauw during the IOP but were changed later to an AIS measurements. The data was viewed by trained scientists on a regular basis to ensure of the well functioning of the devices.

A preliminary classification of the days in event, non-event and undefined days have been done (based loosely on the classifications of Dal Maso et al., 1995 and Hirsikko et al., 2007). Days classified as event day are days on which new particle formation and growth was observed. Non-event days are days on which no formation or growth of aerosol particles is observed. Finally, undefined days are the days that did not fulfill the criteria of event day or those of non-event days. New particle formation and growth event have been observed in all of the 13 EUCAARI stations.

Figure 2 shows the number of days from March to August 2008 in each of the classes described earlier. This has been done for 7 of the 13 stations: Cabauw, Finokalia, Hohenpeissenberg, Hyytiälä, K-Puszta, Mace Head and Po Valley. The monthly event distribution varies from one station to another, which was expected because the stations are from different environments and are in different climates. In K-Puszta, the number of new particle formation events was the highest amongst the studied stations. Finokalia, which is a Mediterranean coastal site, has seen the most non-event days. In Mace Head, particularly, many different types of event have been observed. For example, the classical “banana” type events were observed as well as “apple” and “bump” events (Vana et al., 2008).

**CONCLUSIONS AND FUTURE PLANS**

The measurements have been going on since March 2008 and will keep running until the end of May 2009. More detailed data analysis will be done in the future. For example, growth rates and formations rates can be calculated. To do so, information such as meteorological data and number size distributions is used. The preliminary analysis indicates promising results. The length on the campaign (14 months) will allow interesting seasonal analysis and cover a wide range of weather conditions, environments and climates. New particle formation events have been seen on every one of the 13 selected EUCAARI stations, giving possibilities to approximate the contribution of the events on the total aerosol load in the atmosphere as well as their contribution to cloud formation. This database could, in the future, be integrated to regional and global scale climate models.
Figure 2. The total number of new particle formation event days, non-event days and undefined days during each month of year 2008 for the 7 selected EUCAARI sites: Cabauw (Netherlands), Finokalia (Greece), Hohenpeissenberg (Germany), Hyytiälä (Finland), K-puszta (Hungary), Mace Head (Ireland) and Po Valley (Italy).
REFERENCES


149
INTRODUCTION

Aerosol particles are of major interest for climate research nowadays. Their impact on climate change and their interaction with other climate forcing mechanisms and compounds is not well understood (IPCC, 2007). The lack of understanding is based on the complexity of aerosol particles, due to the variety of chemical and physical properties (Seinfeld, J. H. and Pandis, S. N., 1998). Atmospheric particles are composed of inorganic and organic components. Major inorganic components like ammonium nitrate, ammonium sulfate, and chloride can be detected and their mass contribution can be determined reasonably well by a variety of instruments. However, the major fraction of aerosol particles consists of organic compounds. The vast compositional variety of organic species poses a big challenge in measuring and analyzing aerosol particles.

EXPERIMENTAL

We present measurements of the composition of aerosol particles with an Aerodyne High Resolution Time-of-Flight (HR-ToF) Aerosol Mass Spectrometer (AMS) (Canagaratna, M. R. and Jayne, J. T. et al., 2007) performed during the Intensive Measurement Campaign at CESAR Tower (IMPACT) in May 2008. IMPACT is part of the EUCAARI Intensive Observation Period (IOP) in May 2008. Cabauw is located about 20 km south west of Utrecht and 50 km south of Amsterdam in the Netherlands. The AMS allows real time mass spectrometric measurements of the aerosol particles composition (Jayne, J. T. and Leard, D. C. et al., 2000). Beside an accumulative/bulk analysis of the particles, the AMS provides insights to size dependent composition of particles. This is achieved by size segregation of particles via particle time of flight prior to the mass spectrometric analysis. The AMS used herein is equipped with a high-resolution ToF analyzer from Tofwerk (DeCarlo, P. F. and Kimmel, J. R. et al., 2006).

The measurement extends from 28th of April to 30th of May 2008. Approximately once a week, the measurements were discontinued for three to four hours for calibration purposes. Calibrations performed include aerosol mass calibrations with size selected dried ammonium nitrate (NH₄NO₃) particles, aerosol size calibration with polystyrene latex spheres (PSL) and zero air measurements trough a HEPA filter in the sampling line for approximately 30 minutes. There is an additional data gap on the 2nd of May due to a power failure in the system.

Three distinct meteorological situations were observed during the measurement period. The major situation, ranging almost over the entire measurement period, is the so called regional background situation with air masses originating from Central and Eastern Europe. This situation was disrupted by a scavenged background situation lasting from 17th to 20th of May. Precipitation scavenging and aerosol originating from the North Sea is characteristic for the scavenged background situation. From the 29th of May on, the meteorological background is dominated by long range transport of Sahara dust from North Africa.

RESULTS

Figure 1 shows time series of the major particle components, which are organics, ammonium, nitrate and sulfate and their fractional abundance in the particle. The total detected AMS aerosol mass ranged from approximately 2 µg m⁻³ during the scavenged background period to approximately 30 µg m⁻³ during the Sahara dust period end
of May. The average particle mass concentration during the continental background period ranged from 4 µg m\(^{-3}\) to 10 µg m\(^{-3}\). Sulfate, nitrate, and organics showed diurnal cycles. While nitrate and organics peaked in the early morning, sulfate had its diurnal maximum in the early afternoon. Except for the time from 15\(^{th}\) to 22\(^{nd}\) of May, organics were the major fraction of the particles content. From beginning of 15\(^{th}\) to midday of 17\(^{th}\) and from midday of 21\(^{st}\) to end of 22\(^{nd}\) nitrate and organics were the major components of the particle mass. In the time from midday 17\(^{th}\) to midday 21\(^{st}\) sulfate and organics were dominating the particles composition. In both cases, the two components together accounted for up to 60% of the particle mass in equal parts.

Furthermore, we present comparisons of AMS results versus results of other instruments. The aerosol particle mass measured by the AMS is compared to particle mass derived from size distribution measurements of a Scanning Mobility Particle Sizer (SMPS) operated by TNO. For that comparison, we assume that the particles are spherically shaped and internally mixed. The density of the particles is calculated by accounting for the fractional abundance of ammonium nitrate and ammonium sulfate and their specific densities and assuming a density of 1.2 g cm\(^{-3}\) for the organic fraction. Additionally, we present a comparison of particulate phase nitrate concentration measured with the AMS versus a Proton Transfer Reaction Mass Spectrometer (PTR-MS) (Lindinger, W. and Hansel, A. et al., 1998) operated by IMAU. This specific PTR-MS is optimized for aerosol condensed phase measurements (Holzinger, R. and Hering, S.V. et al., 2008). The two instruments show qualitatively good agreement, indicating that the new approach of measuring aerosol particle composition with a PTR-MS is a promising development.

![Graph](image.png)

**Figure 1:** Fractional abundance of the major components ammonium, nitrate, organic and sulfate in the aerosol particles during the IMPACT campaign.

**OUTLOOK**

In upcoming analysis of our data we will take advantage of the high resolving capabilities of the HR-ToF-AMS. It has two acquisition modes, a single- (V-mode) and a multi-reflection mode (W-mode). This allows us to alternate our emphasis in data acquisition between sensitivity and resolving power. Mass determination and fundamental composition analysis can be performed on V-mode data. W-mode data allows further insights to the actual elemental composition of the organic fraction of the aerosol particles. Our major interest lies on the determination of the oxidation state of the components, which indicates the age of the particles. Additionally, we will extend the analysis of size resolved measurements and use the provided EUCAARI/IMPACT data set for further inter-instrumental comparisons.
REFERENCES


INTRODUCTION

The effect of aerosols on climate is controlled by the number concentration and composition of particles at optically active sizes (~100 nm) and at sizes >50 nm diameter that can act as cloud condensation nuclei (CCN). Most climate change assessments have been made using global models that lack the necessary aerosol microphysics to accurately predict changes in the number size distribution. This limitation on the accuracy of aerosol forcing calculations is well recognised, and has led to the development of several “second-generation” global models that simulate changes in particle number concentration and the particle size distribution (Adams and Seinfeld, 2002, Vignati et al., 2005, Spracklen et al. 2005). However, the development of more advanced global models is hampered by a lack of understanding of what controls particle number concentrations in different environments. At present, the relative strength of different mechanisms contributing to the aerosol budget is not known. Without such fundamental information, long-term changes in aerosol abundance, and hence the effects of aerosol on climate, will remain uncertain.

Earlier, we have used a global aerosol model GLOMAP to show that the vertical aerosol profile can be largely explained with a model including primary particle emissions and a binary homogeneous nucleation of sulphuric acid and water (Spracklen et al., 2005). However, this model still fails to capture the high particle concentrations observed in the boundary layer (BL). An additional particle formation scheme based on cluster activation (Kulmala et al., 2006) needed to be added to explain the BL observations. While significant uncertainties both in particle formation rates and in primary emissions still exist, the model currently produces the observed particle concentrations with reasonable accuracy. The model now captures well the observed particle formation events and the subsequent growth of particles, as well as the observed total particle (CN) and cloud condensation nuclei (CCN) concentrations (Spracklen et al., 2006, 2008). With the full model we were able to provide some first estimates of the global significance of the activation-based nucleation mechanism. Here, we will extend this analysis to provide an estimate of the relative strength of each of the processes contributing to the aerosol budget.

METHODS

The Global Model of Aerosol Processes (GLOMAP) is an offline global chemical transport model incorporating an advanced aerosol microphysics module. The model fully described in Spracklen et al. (2005, 2006). In contrast to other global aerosol models, such as those used in climate simulations, GLOMAP uses a two-moment sectional scheme to represent the particle size distribution, where one is partly hydrophilic including sulphate, sea-salt, black carbon (BC) and organic carbon (OC). The other distribution representing freshly emitted primary carbonaceous particles contains BC and OC and is assumed to be hydrophobic. The hydrophobic OC and BC particles are transferred to the hydrophilic distribution through coagulation and condensation. 20 size sections between 3 nm and 20 μm are used. The model is driven by ECMWF winds and has a spatial resolution of 2.8° x 2.8° with 31 vertical levels between surface and 10 hPa. GLOMAP includes processes of aerosol formation, primary particle
emission, coagulation, condensation, dry and wet deposition, and cloud processing. The anthropogenic and natural BC and OC, primary sulphur and gaseous SO2 emissions are taken from AeroCom database (Dentener 2006). For the sea salt emissions we use the scheme by Gong (2003). The new particle formation in the boundary layer is modelled with the cluster activation theory (Kulmala et al. 2006) using an activation coefficient $A=2\times10^6$. The formation rate for 3nm particles is obtained using the parameterization by Kerminen and Kulmala (2002). Throughout the troposphere assume that particles are also formed via binary homogeneous nucleation of H2SO4 and H2O, for which the parameterized nucleation rates are obtained from Kulmala et al. (1998). In practice, this mechanism takes place only in the upper troposphere. The nucleated particles grow by condensation of sulphuric acid and secondary organics. In the model, the secondary organics are obtained as oxidation products of monoterpenes with an assumed 13 % yield.

Three different model simulations are carried out for the year 2000, from which we obtain the total particle number CN and the cloud condensation nuclei number CCN. Here, CCN is simply defined as all particles larger than a characteristic diameter of 70 nm. The runs include:

1. Run with primary emissions only producing CN(PR) and CCN(PR)
2. Run with primary emissions and BHN producing CN(PR+UTN) and CCN(PR+UTN)
3. Run with primary emissions, BHN and BLN producing CN(PR+UTN+BLN) and CCN(PR+UTN+BLN)

The brackets show the included particle sources, where PR refers to primary particles, BLN to boundary layer nucleation (from cluster activation) and UTN to upper tropospheric nucleation (from binary H2SO4 and H2O nucleation). These runs allow us to separate the contribution of each mechanism to the aerosol budget. The contribution of BL nucleation is obtained from

$$CN(\text{BLN}) = CN(\text{PR+UTN+BLN})-CN(\text{PR+UTN}),$$

$$CCN(\text{BLN}) = CCN(\text{PR+UTN+BLN})-CN(\text{PR+UTN}),$$

And the contribution from UT nucleation is obtained from

$$CN(\text{UTN}) = CN(\text{PR+UTN})-CCN(\text{PR}).$$

$$CCN(\text{UTN}) = CCN(\text{PR+UTN})-CCN(\text{PR}).$$

It should be noted that to some extent the removal of any given particle source from the model will affect the physical and chemical behaviour of the other particles. However, we have tested that the error arising from the neglect of this feedback is very small and can be neglected.

RESULTS

The upper panels of Figure 1 shows the average annual ground level total particles concentrations originating from primary emissions, boundary layer nucleation (activation based nucleation) and upper tropospheric nucleation (binary sulphuric acid-water nucleation). The levels of primary CN follow closely the local emission (BC, OC, primary sulphate, sea salt). The CN produced from BL nucleation follows rather closely the strength in sulphur sources (anthropogenic SO2 and marine DMS). The ground level CN originating from upper tropospheric nucleation, however, is not really affected by the location of emissions. The regional patterns in CN originating from UT tropospheric nucleation are mainly driven by the atmospheric circulation. Highest concentrations can be observed at around 30 degrees from the equator, where the air descends in the Hadley cell.
Figure 1: Upper panels: average annual total particle concentrations for the year 2000 originating from primary emissions, boundary layer nucleation, and upper tropospheric nucleation. Lower panels: corresponding average annual CCN (diameter >70 nm) concentrations.

The lower panels of Figure 1 show how different mechanisms contribute to the CCN concentration. Primary CCN concentrations are nearly equal to primary CN concentrations since primaries are either emitted at CCN sizes or grow rapidly to CCN. As expected, only a fraction of particles from BL nucleation reaches CCN sizes. Ground level particles originating from UT nucleation grow to CCN sizes more effectively than those originating from the boundary layer nucleation, suggesting that they have already grown in size when they reach the ground level. Still, over Antarctica UT nucleation produces large amounts of CN very little CCN. The relative contribution from each of the mechanisms is summarized in Table 1.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Global CN</th>
<th>Global CCN (diameter &gt; 70 nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Emissions</td>
<td>25 %</td>
<td>59 %</td>
</tr>
<tr>
<td>BL nucleation</td>
<td>44 %</td>
<td>11 %</td>
</tr>
<tr>
<td>UT nucleation</td>
<td>31 %</td>
<td>30 %</td>
</tr>
</tbody>
</table>

Table 1: The contribution from different mechanisms to the ground level aerosol budget.

The globally averaged percentage contribution can be, however, somewhat misleading when the spatial importance of different processes is concerned. Figure 2 describes the relative strength of the different processes contributing to the regional aerosol budget. It can be seen that UT nucleation is an extremely significant source of marine particles. In many locations the increased condensation sink caused by the particles from UT nucleation seems to suppress BL nucleation, since the patterns in the CCN(UTN) and CN(BLN) are often opposite.

The significance of UT nucleation as a global source of ground level particles underlines the importance of the vertical transport of particles. The particle lifetime in the upper troposphere is long, and nucleated particles travel long distances before finally dropping to the ground level. It appears that in many remote regions the vertical particle flux of UT nucleated particles dominates over the horizontal flux of boundary...
layer nucleated or primary particles or in-situ formation. For example, CCN(UTN) clearly dominates over other mechanisms in marine regions covered by persistent stratiform clouds.

Figure 2. Maps of the regional contributions of different particle sources to total particle concentrations and cloud condensation nuclei (diameter > 70 nm) concentrations.

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EFFECT OF BOUNDARY LAYER NUCLEATION ON THE CHANGE IN CLOUD ALBEDO FROM 1850 TO 2000

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Keywords: nucleation, cloud droplet number, cloud albedo, global modelling.

INTRODUCTION

Cloud droplet number concentration (CDNC) is controlled by the concentration of aerosol particles large enough to act as cloud condensation nuclei (CCN) (Dusek et al., 2006). The CDNC depends on the concentration, size distribution and chemical properties of CCN and on the updraft velocity defining the maximum supersaturation in a cloud parcel (Nenes and Seinfeld, 2003). Higher CDNC leads to an enhanced cloud albedo (Twomey, 1991). This effect is known as the first indirect effect, and its magnitude is one of the most poorly quantified factors in assessing human impacts on climate (IPCC, 2007).

Observations from several locations around the world suggest that formation of new aerosol particles by nucleation is a frequent phenomenon (Kulmala et al., 2004). These particles can be first detected in the 3-10 nm diameter range, and their subsequent growth to CCN sizes can be followed. Locally, particle formation has been observed to contribute significantly to CCN (Lihavainen et al., 2005). In a previous study we used a global aerosol microphysics model GLOMAP to demonstrate that particle formation in the BL increases the global mean CCN (0.2% supersaturation) concentrations by 3–20% and CCN (1%) by 5–50% (Spracklen et al., 2008). The uncertainties in these values are related to uncertainties in particle formation and growth rates. Thus particle formation is an important, though still quite uncertain, source of CCN in the present atmosphere. But the important question for climate is whether the contribution of particle formation to CCN has changed over the industrial period, which would affect the calculated aerosol indirect forcing. Here, we extend our model simulations of present day CCN to quantify the effect of particle formation on CDNC and cloud albedo under pre-industrial (1850) and present-day (2000) conditions. We use a mid-range estimate for the particle formation rate leading to a 10-20% increase in global present-day CCN.

METHODS

We use the global aerosol microphysics model GLOMAP, which is an extension of the offline 3-D chemical transport model TOMCAT (Chipperfield, 2006). Full details of the model microphysics scheme are described in Spracklen et al. (2005). GLOMAP treats two externally mixed aerosol distributions described by a two-moment sectional scheme with 20 sections spanning 3 nm to 25 μm dry diameter. One of the distributions is partly hydrophilic including sulfate, sea-salt, black carbon (BC) and organic carbon (OC). The other distribution representing freshly emitted primary carbonaceous particles contains BC and OC and is assumed to be hydrophobic. The hydrophobic OC and BC particles are transferred to the hydrophilic distribution through coagulation and condensation of soluble gas-phase species. These species include gaseous H2SO4 and the first-stage oxidation products, which form hydrophilic secondary organic aerosol material with an assumed yield of 13 %. The model has a horizontal resolution of 2.8º by 2.8º with 31 vertical levels between the surface and 10 hPa and is forced by analyses from the European Centre for Medium-Range Weather Forecasts for the year 2000. The same meteorology and oxidants are used. The same meteorology and oxidants are used for 1850 and 2000 runs. The new particle formation in the boundary layer is modelled with the cluster activation theory (Kulmala et al. 2006) using an activation coefficient $A=2\times10^6$. The formation rate for 3nm particles is obtained using the
parameterization by Kerminen and Kulmala (2002). Throughout the troposphere we assume that particles are also formed via binary homogeneous nucleation of H2SO4 and H2O, for which the parameterized nucleation rates are obtained from Kulmala et al. (1998). The cloud drop number concentration (CDNC) is calculated from the time-averaged hydrophyllic particle distribution using the iterative scheme of Nenes and Seinfeld (2003). The schemes take into account the fraction of soluble material in the particles and the number of ions released into the solution. The changes in aerosol, and hence in cloud drop number, are quantified using emissions for 1850 and 2000. The anthropogenic sulfur emissions, accounting also for changes in wildfires, are taken from the inventory of Smith et al. (2004). We use the inventory of Bond et al. (2007) for energy related emissions of BC and OC, and further separate these emissions into biofuel and fossil fuel components using the database of Fernandes et al. (2007). Monthly wildfire BC and OC emissions are from Dentener et al. (2006), where the values for 1850 are obtained by taking a population weighted average of 1750 and 2000 emissions.

The change in cloud albedo during the period is related to the relative change in cloud droplet number. If we assume that there have been no significant changes in the cloud liquid water content or height we can write (Twomey, 1991)

$$\Delta R_c = R_c (1 - R_c) / 3 \ln \left( \frac{\text{CDNC}(2000)}{\text{CDNC}(1850)} \right)$$

where $R_c$ is the initial albedo. According to the above equation, the albedo change depends on the relative change in the cloud droplet number. When particle formation is taken into account, this relative change can be either enhanced or reduced depending on the change in the contribution of particle formation on CDNC. A schematic representation of the effects of particle formation is shown in Figure 1. It shows that particle formation can both enhance and suppress the obtained albedo changes.

![Figure 1](image)

**Figure 1:** Schematic showing how the inclusion of boundary layer nucleation can either increase or decrease the change in cloud albedo ($\Delta R_c$) between 1850 and 2000. (a) Nucleation increases $\Delta R_c$: the fractional impact of nucleation on aerosol number, cloud drop number and cloud albedo is less in 1850 than in 2000. (b) Nucleation decreases $\Delta R_c$: the fractional impact of nucleation on aerosol number, cloud drop number and cloud albedo is greater in 1850 than in 2000. Note that fractional changes in CDNC are always smaller than fractional changes in aerosol number, and fractional changes in $R_c$ are smaller still.

So although the change in aerosol between 1850 and 2000 is much larger than any effect of particle formation, this is not the case for changes in albedo. The effect is exaggerated in the diagram.

To calculate $\Delta R_c$ we assume an initial albedo of 0.35. Although the 1850-2000 changes in albedo are affected by the assumed initial albedo, the assumption does not alter the calculated relative impact of particle formation.
RESULTS

Figure 2 shows the resulting changes in $\Delta R_c$ with and without boundary layer particle formation. The figure shows the averaged full year and Northern hemisphere summer values. The regional patterns of $\Delta R_c$ are quite strongly affected by particle formation. For example, during the northern hemisphere summer particle formation removes the obtained albedo change over large parts of the Arctic region.

Figure 2: The change in cloud albedo with and without boundary layer particle formation (BLPF). Results are shown for an initial albedo $R_c = 0.35$ assuming cloud updraft velocity of $0.4 \text{m/s}$.

The global mean albedo change is predicted to be 3.97% with particle formation and 3.85% without, so the globally averaged impact of particle formation is negligible. This is because particle formation made a nearly equal contribution (16%-13.5%) to global CDNC in both years.

Figure 2 shows the impact of including particle formation in the model on the 2000/1850 $\Delta R_c$ for four Northern hemisphere seasons. Blue areas in Figure 2 indicate regions where the 1850 to 2000 changes in CDNC or $\Delta R_c$ are reduced by including particle formation, and red areas indicate where the changes are increased. It can be seen that boundary layer particle formation has a substantial regional impact on calculated $\Delta R_c$. In large parts of the globe the difference in the obtained albedo change exceeds 50%. The results show a large North-South contrast: particle formation reduces the calculated albedo change in the North and increases it in the South. Results show relatively high seasonal variation, and the largest regional changes are obtained during the Northern hemisphere summer. During the summer the positive albedo change in the Northern hemisphere is greatly reduced, except in North America where particle formation results in a larger positive albedo change. In the South tropics particle formation enhances the obtained albedo change during all seasons. The changes in the Antarctic region are not statistically significant since the obtained albedo change is negligible in all cases.
Of importance for the pattern of radiative forcing is that particle formation enhances the long term increase in CDNC in the persistent stratocumulus regions to the west of Africa and west of South America. Without particle formation, the CDNC change west of South America is predicted to be 18.7% but with particle formation it is 29.0%. This leads to an estimated 49% enhancement in the 1850-to-2000 change in cloud albedo in the region.

These results should be considered as a first attempt to quantify the importance of boundary layer particle formation for long term changes in cloud albedo. It may take time before the fundamental mechanism, or mechanisms, of atmospheric particle formation are resolved. However, since its contribution to CDNC and total particle concentrations appears to be large, best available representations should be utilized when estimating of the effects of aerosols on climate.

Figure 3: The relative error (dΔRc) in calculation of the albedo change if particle formation is neglected. Results are shown for four Northern hemisphere seasons. The updraft velocity is taken to be \( w = 0.4 \text{ m/s} \).

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Airborne in-situ and lidar measurements of European pollution aerosol properties in May 2008: First results of the DLR Falcon deployment during EUCAARI-LONGREX

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Keywords: lidar, aerosol, troposphere, EUCAARI, LONGREX, Falcon, pollution.

INTRODUCTION

The main goal of the EUCAARI project is to investigate the physical, chemical, and radiative properties of atmospheric particles and clouds over Europe. As part of the EUCAARI Intensive Observation Period (IOP) two major aircraft field campaigns were conducted in May 2008, one focusing on aerosol-cloud interaction, EUCAARI-IMPACT, and one on large scale gradients of aerosol properties over Europe, EUCAARI LONGREX (EUCAARI LONG Range Experiment). Two research aircraft operated out of Oberpfaffenhofen airport during EUCAARI-LONGREX: The Falcon 20 research aircraft of DLR, equipped with both lidar and in situ instruments, and the British FAAM BAe-146. The FAAM BAe-146 had the task of characterizing mainly aerosol properties in the boundary layer and therefore of flying in general on low level routes, whereas the DLR Falcon had the task of mapping the vertical aerosol distribution by lidar along the BAe-146 flight path, which required flying on upper airways. Moreover, the DLR Falcon performed stacked vertical profile measurements to characterize in situ aerosol properties in the BL and FT in regions of particular interest (e.g. close to ground observations sites operated during the EUCAARI IOP) in coordination with the BAe-146. This contribution focuses on the first results obtained from analysis of the DLR Falcon data.

METHODS

The scientific payload of the DLR Falcon is summarized in Table 1. It consisted of the DLR lidar system and a combination of in situ instruments for the characterization of aerosol properties (size distribution, non-volatile particle fraction, absorption properties) and transport tracers (carbon monoxide and ozone). The lidar was nadir looking. In normal operation aerosol backscatter profiles were obtained when flying above 8 km altitude. The high spectral resolution lidar (HSRL) operation, allowing for aerosol extinction measurements, was possible in limited measurement regions only, but turned out to be very successful nevertheless. Figure 1 shows DLR Falcon flight tracks flown during the EUCAARI-LONGREX campaign.

RESULTS

The meteorological situation during the first half of the campaign (up to May 14) was characterized by a rather persistent anti-cyclonic system located over central Europe (Figure 2). This situation favoured the build-up of pollution in the boundary layer over central Europe, which is the result of the blocking of long-range transport into central Europe and the absence of precipitation, which could cause removal of aerosol. In this situation a number of Falcon flights could be performed, with two particularly notable cases on May 8 and May 14, where high aerosol concentrations and very high aerosol extinction values were observed. To illustrate this, Figure 3 depicts the vertical aerosol distribution measured by lidar over the British Isles on two flights on May 14, 2008. Results will be further discussed in terms of differences and similarities in aerosol optical and microphysical properties between different flights, air mass origin and transport pathways, and overall level of pollution in the lower, middle and upper...
troposphere during May 2008. Several very successful case studies with almost concurrent vertical sounding by lidar (HSRL) and in-situ vertical profiling of aerosol physico-chemical properties at cloud-free conditions were performed. These cases are expected to be invaluable for closure studies and validation of satellite retrievals. Furthermore, the airborne aerosol measurements performed during EUCAARI-LONGREX will contribute to an observational data base to be used for validation of modelling activities within EUCAARI.

Table 1. List of DLR Falcon instrumentation during the EUCAARI-LONGREX campaign in May 2008.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Measured parameters</th>
<th>Institute</th>
</tr>
</thead>
<tbody>
<tr>
<td>WALES High Spectral Resolution Lidar (HSRL)</td>
<td>extinction profile at 532 nm, backscatter at 532, 925 &amp; 1064 nm, water vapor at 532 nm, aerosol depolarization at 532 nm</td>
<td>DLR</td>
</tr>
<tr>
<td>5-channel CPC system (unheated/heated)</td>
<td>total particle number concentration &gt;10 nm (volatile/non-volatile), ultrafine particles 4-10 nm</td>
<td>DLR</td>
</tr>
<tr>
<td>2-channel Grimm 1.129 OPC (unheated/heated)</td>
<td>particle size distribution 0.25-2 µm (volatile/non-volatile)</td>
<td>DLR</td>
</tr>
<tr>
<td>PCASP-100X</td>
<td>particle size distribution 0.15-1 µm (volatile/non-volatile)</td>
<td>DLR</td>
</tr>
<tr>
<td>FSSP-300</td>
<td>particle size distribution 0.4-20 µm</td>
<td>DLR</td>
</tr>
<tr>
<td>3-wavelength-PSAP</td>
<td>absorption coefficient, Angström exponent</td>
<td>DLR</td>
</tr>
<tr>
<td>New air ion spectrometer (NAIS)</td>
<td>ultrafine particle/ion size distribution</td>
<td>Univ. Tartu</td>
</tr>
<tr>
<td>CO</td>
<td>carbon monoxide mixing ratio</td>
<td>DLR</td>
</tr>
<tr>
<td>Ozone</td>
<td>ozone mixing ratio</td>
<td>DLR</td>
</tr>
<tr>
<td>Falcon &quot;meteorological&quot; data</td>
<td>position, wind, temperature etc., humidity (up to ~8 km)</td>
<td>DLR</td>
</tr>
<tr>
<td>Broad-band radiometer</td>
<td>longwave and shortwave radiation flux</td>
<td>DLR</td>
</tr>
</tbody>
</table>

Figure 1. Map of DLR Falcon flight tracks during the EUCAARI-LONGREX campaign in May 2008. Highlighted are flight sections inside the boundary layer, which indicate the locations where vertical profiles were obtained for in-situ measurements.
Figure 2. Typical meteorological situation encountered during the first half of the EUCAARI-LONGREX campaign. (this example: geopotential and wind field at 850 hPa based on ECMWF forecast data).

Figure 3. Aerosol vertical distribution (backscatter at 532 nm) over British Isles measured by lidar during two flights on May 14, 2008. 
INTRODUCTION

The neutral cluster and air ion spectrometer (NAIS) is an instrument that measures the distribution of naturally charged particles (ions) in the electric mobility range from 3.2 to 0.0013 cm$^2$V$^{-1}$s$^{-1}$ and the distribution of aerosol particles in the size range from 1.5 to 40 nm. Its principal parts are two parallel multichannel mobility analyzers. The first NAIS was built in 2004 as a successor of AIS (air ion spectrometer, Mirme et al., 2007). The spectrometers have successfully been used in studying atmospheric particle nucleation all over the world (Kulmala et al., 2007).

In 2008 a new version of NAIS was developed that would be able to operate on an aircraft at high altitudes, i.e. low barometric pressure. The instrument participated in the EUCAARI LONGREX campaign onboard the DLR Falcon.

MODIFICATIONS REQUIRED FOR FLIGHT

The mobility of a particle changes depending on air pressure. To keep the measured size range of particles constant in varying air pressure, the sheath airflow speed of the mobility analyzer needs to be automatically adjusted as a function of air pressure. The sample airflow also needs to be kept under automatic control to keep the volume flowrate constant for correct concentration measurements regardless of air density.

To allow this control, the airflow system of the NAIS was redesigned to include an air pressure sensor, additional flowmeters and separate pumps for positive and negative analyzer sheath flows and sample flow.

A new data acquisition system was designed to manage the automatic airflow control. Also, a faster 24-bit digital analog converter was used, which improves the measurement rate of the instrument to a maximum of 10 aerosol or ion distributions per second.

These changes will also benefit future ground based measurements with the instrument. Due to the automatic flow control, the instrument will be less affected by pollution of air tract. The new data acquisition system allows to better control the particle chargers and filters.

RESULTS

The NAIS was installed in the DLR Falcon 20. It flew in total about 50 flight hours during the EUCAARI LONGREX campaign.
The first flight (testflight) revealed that the planned sample inlet configuration was unsuitable. The problem was solved by small modification, which made it necessary to manually adjust the instrument during larger altitude changes.

The instrument itself operated as expected. The airflows were correctly adjusted up to 8 km altitude. The sheath flow pumps were unable to provide the required flowrate for higher altitudes, i.e. lower air-pressures. This caused the measurement range of the instrument to shift towards larger particles, but the presence of cluster ions was still visible (Figure 1).

The measurements confirm the principal possibility to study cluster and nanoaerosol at high altitudes with the NAIS.

![Graphs showing ion concentration over time and altitude](image)

Figure 1: Sample results from a flight over Germany and Baltic sea on May 08, 2008.

REFERENCES


Overview of aerosol chemical composition from the BAe-146 during EUCAARI-LONGREX

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Keywords: Chemical Composition, Organic Carbon, Ammonium Nitrate, Black Carbon, Optical Properties, Hygroscopicity

ABSTRACT

The chemical composition of the atmospheric aerosol burden has significant implications for its climate impacts. Specifically, it determines the scattering or absorbing nature of the aerosol and its affinity for water uptake. Measurements of aerosol chemical composition are presented here from the UK Facility for Airborne Atmospheric Measurement (FAAM) BAe-146 research aircraft. These will be linked to the optical and hygroscopic properties of the aerosol burden. The BAe-146 operated in conjunction with the DLR Falcon out of Oberpfaffenhofen, Germany during the EUCAARI LONG Range EXperiment (LONGREX) in May 2008. Science flights were conducted across Western Europe, during a period of anticyclonic circulation in clear sky conditions.

The aircraft employed a suite of aerosol instruments, which resolve the chemical composition, microphysical, optical and hygroscopic properties of the in-situ aerosol population. An Aerodyne compact Time-of-Flight Aerosol Mass Spectrometer (cToF-AMS, Jayne et al., 2000; Drewnick et al., 2005; Canagaratna et al., 2007) measured
the mass of volatile and semi-volatile particulate chemical constituents, as a function of size. These components included organic carbon, nitrate, sulphate and ammonium. Black carbon number and mass, as a function of particle size, were characterised using a Droplet Measurement Technologies (DMT) Single Particle Soot Photometer (SP2, Stephens et al., 2003; Baumgardner et al., 2004).

Organic carbon was found to be ubiquitous across Europe and largely secondary in nature. Ammonium nitrate was found to be a significant component of the aerosol burden. During periods of European outflow, where aerosol was advected across the Netherlands and Belgium into the North Sea, nitrate was seen to be the dominant chemical component of the sub-micron mass. The aerosol scattering profile was closely coupled to nitrate mass concentration. Case studies of aerosol processes and impacts will be highlighted. These include organic carbon source apportionment, assessment of black carbon mixing state and partitioning of ammonium nitrate as a function of the thermodynamic structure of the boundary layer, which exacerbates its optical impact. Such studies will form the basis of subsequent avenues of future research.

REFERENCES

CONNECTIONS BETWEEN NEW PARTICLE FORMATION
AND SULPHURIC ACID IN HYYTIÄLÄ, FINLAND

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Keywords: atmospheric aerosols, nucleation, sulphuric acid

INTRODUCTION
Atmospheric new particle formation has been observed in many different environments around the world (Kulmala et al., 2004). Sulphuric acid has been identified as a key component in this phenomenon, as formation rate of new particles seems to have a linear or square dependence on ambient sulphuric acid concentration. Two nucleation mechanisms, activation and kinetic type nucleation, have been proposed as an explanation for this relationship (Kulmala et al., 2006). In this study we examine the connections between sulphuric acid and particle formation rates observed in a measurement station in Finland during three spring-time campaigns.

MATERIALS AND METHODS
Measurement data used in this study is obtained from the University of Helsinki SMEAR II station located in a rural environment in Hyytiälä, Southern Finland (Hari and Kulmala 2005). Aerosol particle number size distributions have been measured continuously at SMEAR II since 1996 (Mäkelä et al., 1997) with a DMPS (Differential Mobility Particle Sizer) system. The DMPS system operating in Hyytiälä consists of two differential mobility analyzers measuring particle size distributions in diameter range 3–1000 nm (Aalto et al., 2001). Starting from 2003 also charged particle size distributions have been measured with two air ion spectrometers, BSMA (Balanced Scanning Mobility Analyzer) and AIS (Air Ion Spectrometer) (Tammet, 2006 and Mirme et al., 2007). In 2006 a Neutral cluster and Air Ion Spectrometer NAIS was installed at the station (Kulmala et al., 2007). The NAIS measures total particle (both charged and electrically neutral) concentrations in diameter range starting from about 2 nm and extending to 40 nm.

In addition to the continuous measurements at the SMEAR II station, an intensive campaign was carried out during 6.3.–30.6.2007 within the EUCAARI (European integrated project on aerosol, cloud, climate and air quality interactions) project. We will utilize in this study sulphuric acid measurements made during that period. Gas phase sulphuric acid concentrations were measured with a technique utilizing selected chemical ionization and detection with a mass spectrometer. Measurement set-up used in the campaign is described in detail in Petäjä et al. (2008) and references therein.

In this study we are analyzing connections between freshly formed atmospheric aerosol particles and gas phase concentrations of sulphuric acid. Based on the aerosol spectrometer size distribution measurements each day is classified to be either an event day (when we see new particle formation and growth of these particles into larger sizes), a non-event day (when no new particles are seen to appear) or undefined day (when it cannot be determined reliably whether there is new particle formation or not). The classification is made according to the criteria developed by Dal Maso et al. (2005).

Particle formation rates during the events can be calculated from the DMPS or the NAIS measurement data. Here we present results based on DMPS data, as this could be used more reliably on every event day. Formation rates $J_3$ of 3–6 nm particles were calculated from DMPS data with the following formula:

$$J_3 = \frac{dN}{dt} = \frac{dN}{dD3} \cdot \frac{dD3}{dt}$$
\[ J_3 = \frac{dN_{3-6}}{dt} + \text{CoagS}_4 \cdot N_{3-6} + \frac{GR}{3\text{nm}} \cdot N_{3-6}. \]

Here \( N_{3-6} \) represents the number concentration of 3-6 nm particles, \( \text{CoagS}_4 \) is coagulation sink for 4 nm particles and \( GR \) is the growth rate between 3-7 nm. Particle growth rates are calculated from the size distributions by determining the peak concentration in each size range of the measurement instrument and fitting a linear function to these points (Hirsikko et al., 2005). The formation rate of 2 nm particles is calculated from \( J_3 \) using the formula of Kerminen and Kulmala (2002):

\[ J_2 = J_3 \exp(\gamma \frac{CS'}{GR} \left( \frac{1}{2\text{nm}} - \frac{1}{3\text{nm}} \right)) \]

Here \( CS' \) is condensation sink (in \( \text{m}^2\text{nm}^-1 \)) and the coefficient \( \gamma \) is approximately 0.23 \( \text{m}^2\text{nm}^2\text{h}^-1 \).

Measured sulphuric acid concentrations are compared to the new particle formation rates using two proposed nucleation mechanisms (Kulmala et al., 2006). According to the activation type nucleation particle formation rate is linearly proportional to sulphuric acid concentration. In the kinetic type nucleation particle formation rate is proportional to the sulphuric acid concentration squared. These two nucleation mechanisms can be expressed as:

\[ J_{\text{act}} = A \cdot [\text{H}_2\text{SO}_4], \]
\[ J_{\text{kin}} = K \cdot [\text{H}_2\text{SO}_4]^2. \]

The nucleation coefficients \( A \) and \( K \) are determined for each event day by fitting with the method of least squares the \( J_{\text{act}} \) and \( J_{\text{kin}} \) values obtained from the sulphuric acid measurements to particle formation rate \( J_2 \).

RESULTS AND DISCUSSION

There were 54 new particle formation event days during the EUCAARI campaign 6.3.-30.6.2007. On 21 days there was no evidence of new particle formation taking place (non-event days), and 42 days could not be reliably classified as either event or non-event days (undefined days). Sulphuric acid measurement data was available on 30 event days, so that we could use them in our analysis.

On all the event days there was a clear correlation between sulphuric acid concentration and concentration of the newly formed 3-6 nm particles as well as the particle formation rate. On many days it was not possible to reliably determine whether linear or square dependence between sulphuric acid concentration and formation gives better correlation. It might even be possible that the dependence changes during the course of the particle formation event. Because of this both \( A \) and \( K \) coefficients are determined for each event day.

Figure 1 shows the variation of the values obtained for the nucleation coefficients \( A \) and \( K \) during the 2007 EUCAARI campaign and also similarly determined nucleation coefficients on two other springs, 2003 and 2005, when sulphuric acid has been measured in Hyytiälä. It can be seen that both coefficients vary by more than an order of magnitude during each of the campaigns. Comparing the values during different campaigns it can be seen that the activation coefficient \( A \) had higher values in 2003 than in 2005 and 2007. The kinetic coefficient \( K \) on the other hand was clearly smaller in 2005 than in 2003 and 2007. Possible reasons for these differences could be variations in atmospheric conditions between the years, since the nucleation coefficients contain information about the physical and chemical processes related to particle formation. So far we haven't been able to find out clear dependencies of these coefficients on meteorological variables (such as temperature, RH or condensation sink) or basic ambient gas concentrations. Probably also other compounds than sulphuric acid are involved in the first stages of new particle formation. This is supported by the fact that when comparing to the observed growth rates of the newly formed 2-3 nm particles, condensation of sulphuric acid could explain typically only 5-25% of the growth during the EUCAARI 2007 campaign.
Figure 1: Median, mean, quartile and minimum and maximum values of the activation (left) and kinetic (right) nucleation coefficients during three different measurement campaigns in Hyytiälä in 2003, 2005 and 2007.

REFERENCES


INTRODUCTION

Located on the west coast of Ireland, the Atmospheric Research Station at Mace Head is unique in Europe, offering westerly exposure to the North Atlantic ocean (clean sector, 180 degrees through west to 300 degrees) and the opportunity to study atmospheric composition under Northern Hemispheric background conditions as well as European continental emissions when the winds favour transport from that region. The EUCAARI campaign took part between the 10th of May 2008 and the 15th of June 2008. A range of other on-line aerosol instruments was deployed to measure different physical characteristics of the ambient aerosols sampled such as size resolved particle number concentrations (5nm-10µm), Aethalometer, Nephelometer, Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA), cloud condensation nuclei (CCN) and also two particle mass spectrometers (Aerosol Mass Spectrometer HR-TOF-AMS and Aerosol Time of flight Mass Spectrometer ATOFMS). During the 35 days of the intensive field study, two broad periods were clearly identified: the former heavily influenced by long range transport of pollutants from the European continent (10th-31st May), the latter characterized by a much lower aerosol loading with more marine, arctic and south east air masses (1st-15th June). Furthermore, a continuous clean marine period - with Black Carbon always lower than 50nm/m^3 - was identified between 3rd and 7th of June as well as a period characterized by air masses originated in the south west (9th-10th June).

Moreover, several short term events were identified, including 18 coastal nucleation events, five local biomass events (19th and 26th May, 3rd, 7th and 9th of June), four events of high nitrate-containing aerosols regionally transported (16th, 18th, 23rd and 24th of May). Along with in situ measurements, a continuous monitoring of the troposphere was performed by remote sensing instruments such as a CHM15K ceilometer (aerosol profiling and cloud base detection), a MIRA36 Ka-band cloud radar (cloud micro-physics) and a RPG-HATPRO microwave radiometer (humidity and temperature profiler) with infrared channel for cloud base detection. The overall measurements of aerosol size distributions, chemical composition, hygroscopic properties and CCN concentrations associated with the remote sensing ones will elucidate the rule of aerosol on the modification of cloud micro-physics and its radiative properties.
PRELIMINARY RESULTS

During the 35 days of the intensive field study, periods with different air mass source regions were identified, as indicated in Table 1.

<table>
<thead>
<tr>
<th>Periods</th>
<th>Air masses origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>15/05 1200 – 19/05 0000</td>
<td>North East continental Europe polluted air</td>
</tr>
<tr>
<td>19/05 0000 – 21/05 0000</td>
<td>North East UK polluted air</td>
</tr>
<tr>
<td>21/05 0000 – 22/05 1200</td>
<td>France polluted air</td>
</tr>
<tr>
<td>22/05 1200 – 24/05 0000</td>
<td>East continental Europe polluted air</td>
</tr>
<tr>
<td>24/05 0000 – 25/05 0000</td>
<td>France polluted air</td>
</tr>
<tr>
<td>25/05 1200 – 28/05 1200</td>
<td>North Atlantic clean marine air</td>
</tr>
<tr>
<td>29/05 0000 – 03/06 0000</td>
<td>Stagnant polluted air</td>
</tr>
<tr>
<td>03/06 0000 – 08/06 0000</td>
<td>North West Atlantic</td>
</tr>
<tr>
<td>08/06 0000 – 09/06 0000</td>
<td>North Atlantic marine air</td>
</tr>
<tr>
<td>09/06 0000 – 10/06 0000</td>
<td>South West tropical air</td>
</tr>
<tr>
<td>10/06 0000 – 12/06 1200</td>
<td>North Atlantic marine air</td>
</tr>
<tr>
<td>12/06 1200 – 15/06 1200</td>
<td>Arctic marine air</td>
</tr>
</tbody>
</table>

Table 1. Summary of time periods of Mace Head EUCAARI Intensive Campaign with different air masses origin.

A range of on-line aerosol instruments was deployed to measure different physical characteristics of the ambient aerosols sampled, but two particle mass spectrometers were able to provide not only physical but also chemical information on the aerosols in real time. In recent years aerosol mass spectrometry has become available as a powerful tool for the chemical on-line characterization of individual aerosol particles (Murphy, 2007) or small aerosol ensembles (Canagaratna et al., 2007). The ATOFMS (TSI-Model 3800) provides information on a polydisperse aerosol, acquiring precise aerodynamic diameter (±1%) within the range 0.3 to 3 micrometres and individual particle positive and negative mass spectral data in real time. The AMS (Aerodyne Research, Inc.) provides online, real time measurements of the mass of non-refractory components of aerosol particles as function of their size. ATOFMS is capable of single particle analysis, whilst AMS requires the collection of an ensemble of particles to obtain sufficient sample for analysis. The ATOFMS ability to detect single airborne particles can provide valuable particle mixing state information. However, the AMS can quantify the size resolved organic carbon, sulphate, ammonium and nitrate mass loadings of aerosol in the size range between 60 and 600 nm. The ATOFMS collected about 600,000 single particle positive and negative mass spectra. The ATOFMS dataset were analysed with the powerful ART-2a tool, an artificial intelligence algorithm that sorts single particle mass spectra into specific particle type or clusters. About 30 different particle types were identified by the ATOFMS, including for example sea salt, dust, Elemental carbon, biomass, Nitrate-rich and many others.
Two different groups of ATOFMS particle types were found to correlate with air masses back trajectories analysis: the former associated mainly with air masses that had travelled across the European continent before arriving at Mace Head, the latter characterized by air masses with much lower aerosol mass loading originated in the North Atlantic region.

![Graph showing temporal trends of ATOFMS counts and Black Carbon (BC) measurements](image)

**Figure 1.** (top) Hourly ATOFMS counts for cluster type NaCl (pure sea salt) and NaNOx (Sodium Nitrate). Black Carbon (BC) measurements taken with MAAP and Aethalometer (bottom)

Figure 1 shows that the former period is associated mainly with aged reacted sea salt (NaNOx) and high mass loadings of BC (about 350 µg m\(^{-3}\)), while the latter is characterized only by fresh pure sea salt (NaCl) and low levels of BC (about 60 µg m\(^{-3}\)).

**Case study 1: Nitrate aerosol**

During the campaign several spikes of high mass loading of nitrate aerosols were detected. The ATOFMS revealed two different types of nitrate with different degree of mixing state with organic carbon and their temporal trends are shown in Figure 2.
Case study 2: Clean marine period

A continuous period of about 110 hours (almost 5 days) was characterized by clean marine air which originated in the North Atlantic. BC values were always 40 nm m$^{-3}$ and total particle concentrations (>14nm) below 600 particle/cc. Figure 3 shows the AMS mass loadings for the clean marine period, along with SMPS size distributions and growth factors for different sizes. The two main components of the detected mass were nss-sulphate and organics, with levels at about 0.3 $\mu$g m$^{-3}$ and 0.15 $\mu$g m$^{-3}$ respectively. There was very little evidence of nitrate and ammonium. Several observations in clean marine environments indicate that the concentration of primary and secondary aerosol components is driven by the seasonality of oceanic biological productivity (Yoon et al. 2007, O’Dowd et al. 2004). The synergy between the ATOFMS and the High Resolution TOF-AMS will allow elucidating further the organic chemical composition of the marine aerosols and its mixing state.
Figure 3. SMPS size distributions (top) AMS aerosol mass loadings (middle) and HTDMA growth factors for different sizes (bottom) for the clean marine period.

Figure 3 also shows the hygroscopic growth factor (HGF) calculated with the HTDMA. It appears to be a single growth factor mode most of the time. Typical modal GFD,90% is variable but broadly within the range of 1.3 to 1.6, showing no clear size dependence and with little contribution outside the dominant mode but not all the time. Sub-micron particles therefore appear internally mixed with respect to sub-saturated water uptake with growth factors consistent with mixed ammonium sulphate/organic composition.

The AMS size resolved aerosol mass loading for organic, nitrate, sulphate and ammonium are shown in Figure 4a. The size distributions of the sulphate and organics were very similar, with a peak in the mass mode at around 300 nm in vacuum aerodynamic diameter space. Figure 4b instead shows the size distributions for a different period of the campaign where the atmospheric aerosol was characterized by high mass loading of nitrate.

REFERENCES


SEPARATION OF OC AND EC FOR RADIOCARBON-BASED SOURCE APPORTIONMENT OF CARBONACEOUS AEROSOL


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Key words: OC, EC, radiocarbon, source apportionment, thermo-optical.

INTRODUCTION

Radiocarbon is a powerful tracer that enables to discriminate between fossil, \({}^{14}\)C-depleted sources – e.g. traffic – and non-fossil sources – such as biomass-burning and direct biogenic emissions – of carbonaceous aerosol. This latter divides into organic and elemental carbon (respectively OC and EC) fractions, which exhibit very different chemical and physical properties and are not influenced by the same sources. Therefore, isolating them so as to study their radiocarbon content separately appears of major interest.

This separation, which relies on the difference of volatility and chemical reactivity of both fractions, remains a challenge. On the one hand, OC is liable to char during its volatilisation process, thus leading to a partial loss of OC and to a contamination of the EC fraction. On the other hand, the thermal boundary between removal of OC alone and co-volatilisation of OC and EC is blurred and occurs at lower temperatures when inorganic catalysts are present in the sampled aerosol or in the filter composition.

METHODS

Consequently, an optical monitoring of the sample combustion is required for better understanding of those charring and co-volatilisation processes in order to minimise their impact on \(^{14}\)C measurements. We currently investigate the adaptation of the sample preparation procedure described in Szidat et al (2004) to a thermo-optical device (Sunset EC/OC analyser) running under pure oxygen. In this device, the CO\(_2\) resulting from the volatilisation of the different fractions during analysis is quantitatively recovered for radiocarbon analysis. We discuss the development of optimised separation of the main fractions of carbonaceous aerosol using ambient aerosol samples.

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SULFURIC ACID AND OH CONCENTRATIONS IN HYYTIÄLÄ

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Keywords: sulfuric acid, hydroxyl radical, CIMS, atmospheric aerosols, formation.

INTRODUCTION

As demonstrated in a number of investigations (Kulmala et al., 2004), gaseous sulphuric acid plays a central role in atmospheric aerosol formation. A technique for measuring the gas-phase sulfuric acid concentration even down to about \(10^4\) molecules cm\(^{-3}\) has already been available for more than a decade (Eisele and Tanner, 1993). As a result, a number of field campaigns have been performed that allow us to look at connections between the gas-phase sulphuric acid concentration and aerosol formation or growth rates. Although sulfuric acid seems to be a key component in the formation (e.g. Weber et al. (1997); Fiedler et al. (2005); Sihto et al. (2006), there are strong indications that condensing vapors other than sulphuric acid are frequently needed to explain the observed particle growth rates (Held et al., 2004; Fiedler et al., 2005).

The aim of this study is to present results from a field campaign conducted in Hyytiälä, Finland. We measured gaseous phase sulfuric acid and hydroxyl radical concentrations with a Chemical Ionization Mass Spectrometer (CIMS). In addition, several proxy variables were explored and compared with the measured sulfuric acid concentrations. For comparison chemistry box-model (Boy et al., 2005) was used to calculate sulfuric acid concentrations as well.

EXPERIMENTAL SETUP

Measurements presented in this study were conducted at SMEAR II (Station for measuring Forest Ecosystem-Atmosphere Relations) located in Hyytiälä, Southern Finland (Hari and Kulmala, 2005). These observations were done as a part of ”European Integrated project on Aerosol Cloud Climate and Air Quality Interactions” (EUCAARI) project field campaign.

Selected Ion Chemical Ionization Mass Spectrometer, SICIMS

Sulfuric acid in the gas phase was measured with a technique utilizing selected chemical ionization and subsequent detection with a mass spectrometer. The CIMS instrument was operated inside
a seatainer, approximately 400 m southwest of the main SMEAR II measurement station. The measurements were conducted between March 24 and June 28, 2007.

Measurement of sulfuric acid with the CIMS consists of several steps, including sample transport, chemical ionization, ion reactions, mass filtering and signal detection. Concentration of $H_2SO_4$ is calculated from the measured ion signals as

$$[H_2SO_4] = C \cdot \frac{HSO_4^-}{NO_3^-},$$

where C is directly measured calibration coefficient (Mauldin, III et al., 1999). One measurement cycle is completed in 30 seconds. A nominal detection limit of the CIMS instrument is $5 \cdot 10^4$ molecule cm$^{-3}$ (Mauldin III et al., 2001) for a 5 minute integration period. A more detailed description of the technique is presented in Tanner et al. (1997); Mauldin III et al. (1998) and references therein.

The measurement of hydroxyl radical relies on the detection of isotopically labeled sulfuric acid with CIMS-technique. More details can be found in (Eisele and Tanner, 1991, 1993; Tanner et al., 1997; Mauldin III et al., 1998).

During a CIMS measurement cycle, $H_2SO_4$ was measured 10 times followed by 20 measurements of combined OH and $H_2SO_4$ concentrations each lasting typically 30 s. The concentrations were averaged over 5 minutes.

Proxy calculations and model simulations

Ambient sulfuric acid concentrations is depicted by its sinks and sources. Sulfur dioxide is the main precursor as it oxidizes to sulfuric acid through radical reactions and the main sink is collisions with aerosol particles. To gauge sulfuric acid source rate indirectly, we calculated several proxy concentrations based on measured gaseous phase concentrations, solar radiation and measured aerosol size distribution acting as a condensation sink for the sulfuric acid molecules. More details on the used proxies and their comparison can be found from Petäjä et al. (2008).

A pseudo-steady state chemical box-model was used to calculate sulfuric acid concentrations. This model was successfully verified against measured sulfuric acid data in Hyytiälä (Boy et al., 2005).

RESULTS

Sulfuric acid had a clear diurnal cycle as depicted in Fig. 1. Typical daily maximum sulfuric acid concentration was $7.8 \cdot 10^5$ molecules cm$^{-3}$ for 30-min averaged data. During new particle formation events days the sulfuric acid concentration reached higher concentrations, as the grand-averaged mid-day concentration reached values up to $1 \cdot 10^6$cm$^{-3}$. During non-event days the amplitude of the diurnal cycle was diminished, reaching only $3.4 \cdot 10^5$ molecules cm$^{-3}$. Also the night-time concentrations were typically lower during days without new particle production.

Correlation of gas-phase sulfuric acid concentrations with number concentration of the nucleation mode particles was already discovered in the 1990s (Weber et al., 1996). Fig 2 presents aerosol number concentration between sizes 3 to 10 nm as a function of measured sulfuric acid concentration. The upper figure contains all the campaign data and revealed a slope of 1.27 whereas constraining the data only to clear new particle formation event days produced a slope of 1.49. Previously in Hyytiälä values between 1 and 2 are reported (Sihto et al., 2006). Even further confinement of the data during two new particle formation event days lead to value of $1.99 \pm 0.11$, when the calculated formation rate of 1 nm particles was plotted against the sulfuric acid concentration (Kuang et al., 2008).
Fig. 2 also reveals a striking difference between results obtained using a standard least-squares fitting and Williamson-York (Williamson, 1968; York, 1969) fitting procedure. The latter takes into account the fact that there are errors in the data points both in x and y-direction. As shown by Cantrell (2008), the accuracy of the slope acquired with the Williamson-York method improves with the number of data points, which is not the case with the standard least squares fit with prominent errors in the x-variable. In addition, the Williamson-York fit proved to provide results which were invariant with respect to exchange of x and y whereas the standard, unweighed least squares method was not.

CONCLUSIONS

Sulfuric acid was measured with Chemical Ionization Mass Spectrometer (CIMS) in Hyytiälä, Finland, in March-June, 2007. Clear differences in sulfuric acid concentrations were detected during new particle formation event days and non-event days. Measured sulfuric acid concentrations correlated well with two proxy variables as well as detailed pseudo-steady state chemical model results (Petäjä et al., 2008).

The measured sulfuric acid concentration correlated with detected aerosol number concentration with a slope of 1.27 during all available data increasing up to value of 1.49, when only clear new particle formation event days were included. Furthermore, the correlation analysis underlined that the fitting results obtained with least squares methods should be used with caution, if the errors in x and y direction are comparable as pointed out by (Cantrell, 2008).

ACKNOWLEDGEMENTS

This work has been partially funded by European Commission 6th Framework programme project EUCAARI, contract no 036833-2 (EUCAARI). Also support by the HERC project ”Urban and rural air pollution response of ecosystem and society (URPO)” is acknowledged. TP gratefully acknowledges financial support of Academy of Finland via project ”Importance of in-situ measured sulfuric acid on the aerosol formation and growth in the atmosphere”, decision number 120530.

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Figure 1: Examples of sulfuric acid (upper panel) and hydroxyl radical (bottom panel) timeseries during EUCAARI field campaign in Hyytiälä. Open squares present measured values, plus-sign modeled, open circles, dots and crosses different proxy concentrations. The bar at the bottom depicts particle formation event days.
Figure 2: Correlation of particle number concentration in the size range 3 to 10 nm and measured sulfuric acid concentrations. Upper figure presents all available data as 30-min averages whereas the bottom figure depicts only data measured during class I (Dal Maso et al., 2005) event days. Dashed line is a least squares fit and the solid line represent Williamson-York fit assuming errors both in x- and y-direction.


Achieving an improved sulphur cycle in the HadGEM model through on-line calculation of oxidant concentrations

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Despite the importance of aerosols for climate predictions, the Level of Scientific Understanding of modelled concentrations and climatic effects of aerosols has been assessed to be 'medium-low' for the direct effect and 'low' for the indirect effect (Forster et al., 2007). It is therefore necessary to consider ways to improve the representation of aerosols in climate models.

In the Hadley Centre Global Environment Model (HadGEM1; see, e.g., Martin et al. 2006, Ringer et al. 2006 and Johns et al. 2006), sulphate aerosol is produced from reactions of dimethyl sulphide (DMS) and sulphur dioxide (SO2) with oxidants (OH, H2O2, O3 and HO2). Concentrations of these oxidants are supplied to HadGEM1 as monthly-mean fields originally obtained from the STOCHEM Chemistry Transport Model (CTM) (see, e.g., Collins et al. 1997 and Stevenson et al. 1998). These oxidant concentrations do not vary from one year to the next, and have no diurnal cycle and no interactive dependence on climate. This method is similar to those used by Feichter et al. (2004) and Pham et al. (2005). Other authors (e.g., Berglen et al. 2004, Spracklen et al. 2005) have studied the sulphur cycle with CTMs which use on-line oxidants, but these models are driven by off-line meteorological data.

Rae et al. (2007) studied the effects on sulphate aerosol in HadGEM1 of changing the input oxidant concentrations from present-day values to values consistent with late 21st century predictions of emissions and climate. They compared this with the effects of changing the climate boundary conditions (sea surface temperature and sea ice fraction) and greenhouse gas concentrations in the model to predicted late-21st century values, while holding oxidant concentrations at present-day levels. They found that changing the oxidants alone led to changes in sulphate aerosol burden of a comparable magnitude to the changes induced by changing the climate boundary conditions and greenhouse-gas concentrations, and concluded that it is important to represent oxidant changes due to changes in emissions and climate in future climate scenarios. This requires on-line calculations of oxidant concentrations, as in the work of Unger et al. (2006), i.e., a fully-coupled climate-chemistry-aerosol model.

The United Kingdom Chemistry and Aerosols (UKCA) project is a collaboration between researchers in the Met Office Hadley Centre and in various UK universities to develop a fully-coupled climate-chemistry-aerosol model. When complete, the model will comprise a tropospheric chemistry scheme, a whole-atmosphere chemistry scheme (including stratospheric chemistry), and an aerosol scheme. UKCA will bring many benefits compared to current models, including full coupling between climate, chemistry and aerosols; a whole-atmosphere chemistry model (as opposed to separate tropospheric and stratospheric models); and an improved aerosol scheme. The UKCA model will therefore address the lack of coupling between climate, oxidant concentrations, and sulphate aerosol production discussed by Rae et al. (2007).
HadGEM2-ES is a new Earth System model currently under development in the Met Office Hadley Centre. It uses as its basis the coupled Atmosphere-Ocean model HadGEM2-AO, the successor to HadGEM1. The UKCA chemistry scheme has been implemented in HadGEM2-ES, but the UKCA aerosol scheme is still being developed. Because of this, in HadGEM2-ES the UKCA tropospheric chemistry has been coupled to the existing HadGEM2-AO sulphur-cycle scheme, so that the production of sulphate aerosol in HadGEM2-ES will be driven by oxidant concentrations calculated on-line at each timestep by UKCA, rather than by off-line monthly mean fields. This has the advantage that the effects of climate and meteorology on oxidant concentrations will be represented, as will the diurnal cycle. The coupling will allow the investigation of climate-chemistry-aerosol feedbacks in a way that was not possible with the previous model set-up. Such investigation is important, as the magnitudes of these feedbacks, and their spatial and temporal variations, are still highly uncertain.

Here, we will describe the coupling of the UKCA tropospheric chemistry scheme to the UM sulphur cycle to allow on-line oxidant concentrations to be used in the calculations. We will examine the global and zonal effects that the introduction of such a coupling has on modelled reaction budgets, SO$_2$ and sulphate concentrations, and aerosol optical depths; we will then validate the model results with surface observations. Finally, we will discuss the benefits and potential uses of the new scheme.

References:


GLOBAL MODEL SIMULATIONS OF PARTICLE CONCENTRATIONS OVER EUROPE DURING THE EUCAARI INTENSIVE OBSERVATION PERIOD

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INTRODUCTION

Tropospheric aerosols play an important role in the global climate through their influence on the Earth’s radiation balance. The alteration of the Earth’s radiative balance by atmospheric aerosols is a major uncertainty in assessments and predictions of climate change on both global and regional scales (Forster et al., 2007; Haywood and Boucher, 2000; Penner et al., 2001). In order to understand the impact of aerosol on climate we must understand how anthropogenic emissions alter the size and number distributions of atmospheric aerosol. In the EUCAARI project we aim to improve global model simulations of particle number concentrations and size distributions and understand the sources of particles from primary emissions and nucleation. Here, we use observations from the EUCAARI LONGREX and IMPACT intensive observation periods to test the Global Model of Aerosol Processes (GLOMAP) over the European domain.

The EUCAARI Project

The European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) is a project within the EU's Sixth Framework Program, focussing on aerosol particles and their effect on regional air quality and climate. The EUCAARI consortium consists of 48 partners from 25 countries and is coordinated by the University of Helsinki. The key objectives of EUCAARI are:

(I) Reduction of the current uncertainty of the impact of aerosol particles on climate by 50% and quantification of the relationship between anthropogenic aerosol particles and regional air quality.

(II) Quantification of the side effects of European air quality directives on global and regional climate, and provide tools for future quantifications for different stakeholders.

The EUCAARI project consists of 21 Work Packages (WPs), divided into 5 key elements: 1. Emissions and Formation, 2. Transport and Transformation, 3. Climate and Air Quality Effects, 4. Project Infrastructure, and 5. Integration and Impacts. As part of these work packages, new measurements made on a range of platforms (including ground-based, aircraft and satellite) will be integrated with existing data to produce a global consistent dataset with the highest possible accuracy. Offline models (chemical trajectory models and 3D chemical transport models) forced by actual synoptic fields will be improved by evaluating new model schemes against specific observations from the dataset. Ultimately, these new model schemes will be integrated into global climate models, enabling a better understanding and quantification of the impacts of atmospheric aerosol on climate.

At the University of Leeds we are contributing to work packages 2.5 and 3.3. WP 2.5 is focussing on global/regional scale aerosol particle number, in particular the relative contributions of natural and anthropogenic sources as well as primary and secondary sources to particle number concentrations over Europe. WP 3.3 is concentrating on the development and testing of new parameterisation of aerosol
processes for global and regional models, aiming for more realistic representation of aerosols and aerosol-cloud interaction in climate models to better quantify the direct and indirect effects. We are using a global off-line chemical transport model (described below) to compare against specific observations made during the EUCAARI Intensive Observation Period in May 2008.

**The GLOMAP Model**

The Global Model of Aerosol Processes (GLOMAP) is a global chemical transport model (CTM) that simulates the evolution of size and composition resolved aerosols, including their interaction with trace gases and clouds. We are interested in exploring the fundamental processes that control aerosol properties in all parts of the atmosphere with the ultimate aim to better constrain the effect of aerosol on climate.

The host model for GLOMAP is the TOMCAT global 3-D off-line Eulerian CTM (Chipperfield et al., 1993; Stockwell and Chipperfield, 1999). Large scale atmospheric transport and meteorology in TOMCAT is specified from European Centre for Medium-Range Weather Forecasts (ECMWF) analyses, updated every 6 hours. The host model can be run at a range of resolutions and with different options for physical and chemical parameterisations. These options include a comprehensive tropospheric chemistry scheme with over 40 species. Currently in GLOMAP we are using a reduced sulphur cycle scheme and prescribed oxidant fields from a full TOMCAT tropospheric chemistry run. The sulphur scheme includes the main reactions controlling gas phase abundances of SO2, DMS, DMSO, MSA and H2SO4.

GLOMAP includes primary SO2 emissions from anthropogenic sources taken from the IIASA inventory (Cofala et al, 2005), and volcanic sources obtained from Andres and Kasgnoc (1998). Oceanic DMS emissions are calculated using the monthly mean seawater DMS concentration database of Kettle et al. (1999) and the sea-air exchange parameterization of Nightingale et al (2000). Size-resolved sea salt emissions are calculated either using the equations of Gong (2003) or the more recent formulation of Martensson et al. (2003) based on 10m wind speeds and sea surface temperature. Emissions of biogenic monoterpenes are included as in the GEIA 1b inventory (Guenther et al, 1995).

The aerosol particle types included in the GLOMAP model are: sea spray, sulphate aerosol, elemental carbon, organic carbon, dust, and a simple scheme for secondary organic material based on monoterpane oxidation products. Natural sources of primary aerosol include volcanic sulphate (2.5% of emitted SO2) and sea salt aerosol following Gong (2003). Primary anthropogenic sulphate is emitted as 2.5% of IIASA SO2 from industrial, power-plant, domestic, shipping, road transport, off-road sources following Cofala et al (2005). Secondary sulphate particles are formed through binary homogeneous nucleation above the BL (Kulmala et al., 1998; Spracklen et al., 2005) as well as through particle formation within the BL. Elemental carbon and organic carbon are emitted solely as primary aerosol particles from both anthropogenic sources (fossil fuel and bio-fuel burning following Bond (2004)) and from biomass burning (van der Werf et al., 2003).

The aerosol particles undergo microphysical processes (coagulation, condensational growth and in-cloud processing) that alter the aerosol number size distribution in the model. The processes of dry and wet deposition act to remove the aerosol particles. The aerosol fields in GLOMAP are generated from an initially aerosol free atmosphere. The model is ‘spun-up’ for three-month simulation time to allow the processes of emission, processing and removal to produce a realistic aerosol distribution.

New particle formation in the free troposphere is treated using the binary homogeneous H2SO4-H2O nucleation scheme of Kulmala et al. (1998). GLOMAP attempts to explicitly simulate the competition between nucleation of new particles and the condensational growth of pre-existing aerosol. A range of nucleation rates from the literature have been implemented in the model. Recent advancements have meant that GLOMAP now includes nucleation schemes appropriate for the boundary layer (Spracklen et al., 2006). Since the particle formation rate observed in the BL greatly exceeds the binary homogeneous nucleation rate of sulphuric acid particle formation (Kulmala et al., 1998; Vehkamäki et al., 2002), another mechanism is employed in the model for continental boundary layer conditions. The nucleation mechanism, based on an analysis of extensive observations of particle formation in the BL, assumes molecular clusters form at a rate proportional to the gaseous H2SO4 concentration to the power of 1.
**GLOMAP-bin/-mode.** There are two varieties of the GLOMAP model, GLOMAP-bin and GLOMAP-mode, differing in the way in which they treat the aerosol size distribution. GLOMAP-mode uses log-normal modes defined in terms of particle number and masses of each chemical component. Four movable size modes are used to represent typical nucleation, Aitken, accumulation and coarse size ranges. These modes can be described as various internal and external mixtures. GLOMAP-bin on the other hand uses a size bin scheme with a flexible number of bins geometrically spaced. The primary aerosol quantities that are affected by microphysical processes are the molecules of each condensed species per particle and the number of particles per bin. The aerosol size distribution is simulated in GLOMAP-bin via the moving-centre scheme of Jacobson (1997), using size sections (bins) to represent the aerosol distribution with 2 moments simulated per bin (mass per particle and number concentration in a section). Typically, we use 20 or more size bins spanning dry diameters from about 1 nm to 25 µm.

By implementing both the simple and complex aerosol schemes in the same host CTM (TOMCAT) both model types can be compared against the same observations and each other. A CTM is an ideal model to compare against observations because it uses “real” meteorology. For comparing with observations of aerosol particle number concentrations and how atmospheric processes affect the aerosol size distribution, GLOMAP-bin is the more suitable model since it makes no a priori assumption about the shape of the size distribution. On relatively short timescales, GLOMAP-bin is ideal for comparison against specific observations where there is detailed information on the size distribution or particle number. For this reason GLOMAP-bin has been employed in this study.

**METHOD**

During the LONGREX and IMPACT intensive field campaigns in May 2008, GLOMAP was setup to provide output every hour over a regional (European) domain (Fig. 1). All the results in the present work have a horizontal resolution of 2.8 x 2.8 degrees and 20 vertical levels from surface to 10 km.

Figure 1 shows the modelled surface-level concentration of particles larger than 3 nm diameter (condensation nuclei, CN) on May 8, 2008. We compare two model runs with and without boundary layer nucleation. Nucleation in the boundary layer is simulated according to Spracklen et al. (2006; 2008) assuming that the formation rate of 1 nm clusters is proportional to the gas phase concentration of sulphuric acid:

\[ j_{\text{1nm}} = A[H_2SO_4] \]

where A is a rate coefficient (assumed to be $2 \times 10^{6}$ s$^{-1}$).
The impact of boundary layer nucleation varies highly from region to region. There appears to be very little change in CN number concentration over central Europe between the model run with BL nucleation and the model run without. In contrast, there is a factor of 4 difference in CN number concentration over Finland and a factor of 2 over Eastern Europe between the model runs. These results suggest that nucleation may not have been an important source of particles over central Europe during the polluted early campaign period, but may have been quite important in eastern and northern Europe. Analysis of aircraft and ground station observations will be needed to confirm this model prediction.

Figure 2 compares the modelled CN concentration with observations at Cabauw made using the Helicopter-borne ACTOS instrument of Siebert et al. Concentrations are typically ~1000-1500 cm\(^{-3}\) and agree well with the observations except for a brief period around 8:10 UTC. This peak in concentration in the observations of up to ~9000 cm\(^{-3}\) is not captured by the model. Further work is needed to determine whether this is a nucleation event and whether it impacts the general background CN during the period.
FUTURE WORK

Our research will focus on the general pattern of particle number and the size distribution during the campaign period. We wish to determine the extent to which nucleation is required to explain the observed CN and CCN concentrations. CN data have been obtained from both the DLR Falcon, involved in the LONGLEx campaign; and from the ACTOS instrument involved in the IMPACT campaign. Initially we will use these datasets to do a gross comparison of measured CN number concentrations with the model.

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LONG TERM DIRECT MEASUREMENTS OF AEROSOL SINGLE SCATTERING ALBEDO IN A PRISTINE SITE IN AMAZÔNIA

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Keywords: aerosol, Amazon, albedo, scattering, absorption, organic aerosol

INTRODUCTION

The Amazon tropical forest constitutes a complex ecosystem, in which the biosphere and the atmosphere are linked through the exchange of aerosol particles and trace gases. As a result of the intense convective activity typically observed in the tropics, these atmospheric constituents can be transported over large distances, in a way that the forest may act as a natural global source of biogenic compounds. In natural conditions, the Amazonian aerosols come from biogenic sources, with 70-80\% of the mass on the coarse mode.

A number of intensive experiments for aerosol characterization have been conducted in the Amazon under the scope of the LBA project (Large Scale Biosphere Atmosphere Experiment in Amazonia) (Andreae et al., 2002; Davidson and Artaxo, 2004). Nevertheless, intensive experiments that usually last from weeks to a couple of months are not enough to completely understand some aspects of the Amazonian biogenic aerosol. For example, new particle formation has not been consistently observed in the area, despite of the high emissions of potential gas-phase precursors (VOC). Another question is related to the effect of biogenic and biomass burning aerosols on the radiation budget. This paper shows preliminary results from a long term aerosol experiment in a pristine area in the Amazon forest. As cooperation between the University of São Paulo (Brazil), the IFT-Leipzig (Germany), the Lund University (Sweden), and the State University of Amazonas (Brazil), measurements of aerosol optical properties (scattering, absorption), size distribution and elementary chemical composition have been made since February 2008. This long term experiment is planned to be held for two years.

EXPERIMENTAL

Field measurements have been made since February 2008 at the Cuieiras forest reserve, 60 km NNW of Manaus in Central Amazonia. The site is relatively undisturbed, as the prevailing trade winds blow over vast expanses of intact tropical forest before reaching the measurement tower (TT34), located at km 14 of the ZF2 access road. Inlet lines run from the measurement level (45m, ~10 m above tree height) to a ground-based lab, climatically controlled. A drier on the inlet line keeps the relative humidity roughly constant.

Aerosol scattering measurements have been measured with a TSI-3563-Nephelometer and with an Ecotech-M9003-Nephelometer, for the sake of comparison and validation of data. Aerosol
absorption have also been double measured by similar (but not identical) equipment: 7-lambda Aethalometer (Magee Scientific) and MAAP-CARUSSO. The main difference between these two absorption instruments is that MAAP measures not only absorption through a filter, but also measures the angular reflection to account for filter-particle interactions (Petzold et al., 2005). Two aerosol spectrometer systems have been used: a TSI-3936-SMPS and a lab-made DMPS developed at the Lund University. Number concentrations have been measured with a TSI-3785-CPC optical particle counter. Stacked Filter Units (SFU) have been used to collect fine mode ($D_p < 2.0 \mu m$) and coarse mode ($D_p > 2.0 \mu m$) aerosols during daytime (7 am to 5 pm) and nighttime (5pm to 7 am) periods. Nuclepore filters have been analysed for particulate mass, black carbon and elemental composition.

PRELIMINARY RESULTS

The simultaneous measurement of scattering and absorption coefficients makes it possible to calculate the aerosol single scattering albedo ($w_0$). Data from TSI-Nephelometer and from MAAP have been used on these calculations. The TSI-Nephelometer measures scattering coefficients at 440, 550 and 650nm, whereas the MAAP instrument measures absorption at 670nm. Thus, it is necessary to estimate the coefficients at a common wavelength. For later intercomparisons, we chose to calculate the albedo at the same wavelengths used by the Aeronet sun photometers (440, 675, 870, 1020nm).

The spectral behavior of the aerosol scattering coefficient was estimated applying linear and quadratic fits to the data measured at three wavelengths:

$$\ln(\sigma_{\text{scatt}}(\lambda_i)) = a_0 + a_1 \ln \lambda_i$$

$$\ln(\sigma_{\text{scatt}}(\lambda_i)) = a_0 + a_1 \ln \lambda_i + a_2 (\ln \lambda_i)^2$$

where $\lambda_i = 450, 550, 650$ nm; $\sigma_{\text{scatt}}(\lambda_i)$ is the measured scattering coefficient at each wavelength; $a_0, a_1, a_2$ are the parameters of the fittings. The parameter $a_0$ is related to the Angstrom’s turbidity coefficient ($\beta$); $a_1$ is related to the Angstrom exponent ($\alpha$); $a_2$ is defined as the curvature term (Schuster et al., 2006). In most of the cases, the linear fit was used to calculate scattering coefficients at the desired Aeronet wavelengths. The quadratic fit was applied only when the linear fit was not considered satisfactory ($R^2<0.8$). On the other hand, the spectral behavior of aerosol absorption coefficient was estimated using a simple approximation in which the absorption coefficient falls with $\lambda^{-1}$ (Strawa et al., 2006).

Figure 1 shows the time series of calculated aerosol single scattering albedo at 440 nm, between February and June 2008. In average, the aerosol albedo is 0.88. That is in accordance with the fact that the Amazonian biogenic aerosol is expected to have a very high albedo, as the Black Carbon concentrations are expected to be low. No diurnal variation was observed for the albedo.

In a coming paper, aerosol albedo data will be compared to aerosol mass concentration, as well as to measured aerosol size distributions and elementary composition. This analysis may provide insights about the influence of aerosol physical-chemical properties and dynamic processes over aerosol optical properties.
Figure 1: Aerosol single scattering albedo (440nm) in a pristine area in the Amazon forest.

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MULTI-PLATFORM OBSERVATIONS OF CLOUD CONDENSATION NUCLEI DURING EUCAARI

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Keywords: cloud condensation nuclei, supersaturation, aerosol sources, boundary layer mixing

INTRODUCTION

Since the introduction of IPCC (Intergovernmental Panel on Climate Change) nearly three decades ago, the uncertainty of the impact of anthropogenic aerosols has remained the least constrained radiative forcing component in understanding global climate change [IPCC, 2007]. Such climate impacts, known as direct and indirect effects are, however, still poorly understood, in part because there are relatively few in-situ observations and the magnitude of these aerosol effects varies regionally depending on the sources of aerosols and their physicochemical properties. Aerosols are generally considered to exert a cooling effect at the earth’s surface by directly scattering incoming solar radiation back to space [Charlson et al., 1992] or influencing cloud properties such as enhancing cloud albedo [Twomey, 1974]. Cloud condensation nuclei (CCN) are the subset of aerosol that becomes cloud droplets. Hence, to reduce the uncertainty of the impact of aerosol particles on the climate, the European Integrated project on Aerosol Cloud Climate and Air Quality Interactions (EUCAARI) intensive integrated multiple aircraft and ground stations to quantify the sources and sinks of regional aerosol and their physical and chemical transformations with respect to their cloud-forming potential.

METHODS

During EUCAARI-IMPACT (Intensive Observation Period at Cabauw Tower) and LONGREX (Long Range Experiment), four CCN counters were deployed between ground-based sites and airborne platforms. Such multi-platform observations provide a unique opportunity to:

- identify the physico-chemical properties that dictate CCN activation and their evolution over the European continent
- identify the major sources of cloud-active aerosols in Europe
- quantify the vertical distribution of CCN and relate the in-situ measurements to remote sensing observations
- study the interaction of aerosols and cloud microphysical properties

Table 1 lists the deployment of CCN instruments and their modes of operation during the EUCAARI intensive campaigns in May 2008. The suite of instrumentation on the ground and in the aircraft, include aerosol size distributions, size resolved-chemical composition, lidar, and cloud microphysics, compliment the CCN observations and provide independent assessment of the cloud-forming potential of aerosols, their mixing in the planetary boundary layer and their interactions with clouds over Europe.
Table 1. Deployment of CCN instruments during the IMPACT and LONGREX experiments

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<th>Ground-based CCN measurements</th>
<th>Airborne CCN measurements</th>
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| R. Boers (KNMI)              | G. Roberts (Météo France) |
| Cabauw Tower                 | Cabauw Tower              |
| DMT-CCN                      | mini-CCN                  |
| 0.1% < S_c < 1%              | 0.15% & 0.43% S_c         |
| 400 m                        | 0.22% S_c; 0 < z < 4000 m |
| 0.07 and 0.2% S_c            | 0.07 and 0.2% S_c; 0 < z  |
| 6000m                        |                           |

PRELIMINARY RESULTS

The time series of CCN measurements in Figure 1 illustrates the evolution of the CCN spectra at the Cabauw tower during EUCAARI-IMPACT. Three major features of this time series correspond to the major sources of aerosols during the experiment. Based on back trajectory analysis [Draxler and Hess, 1997], the periods of low CCN concentrations (N_{CCN}) at the beginning of the experiment and around 19 May are related to air masses with origins from the North Sea. The mean NCCN at 0.3% S_c (N_{CCN,0.3}) of 500 cm⁻³ is relatively low compared to the rest of the experiment as a result of the relatively clean origins and precipitation scavenging associated with these air masses. The periods 3-16 May and 23-29 May represent the regional European aerosol background with N_{CCN,0.3} ~ 2000 cm⁻³. Aerosol origins during this period are from Central and Eastern Europe and no precipitation scavenging occurred for several days prior to their arrival at Cabauw. At the end of the experiment, there was a large increase in CCN concentrations related to the long-range transport of Saharan dust and pollution from central and southern Europe. The highest levels of N_{CCN,0.3} ~ 6000 cm⁻³ were observed during this period. These elevated CCN concentrations suggest that aerosol particles have been cloud-processed or undergone chemical transformations that have enhanced their CCN activity. The CCN spectra (Figure 2) highlight the large differences between each of the major sources of aerosols during EUCAARI-IMPACT.

In addition to the time series of CCN spectra (Figure 1), size distributions of aerosol particles and CCN at two supersaturations (0.15% and 0.43%) provide yet another way of assessing the relationship between size and chemistry of CCN active particles (Figure 3). In general, the trends for CCN number distributions follow the changes in aerosol number distribution. For example, the relatively low N_{CCN} (and small CCN size distribution) on 20 May (Figure 3) are largely driven by the small aerosol sizes during this period (mean diameter ~ 40 nm). However, notable shifts in the CCN size distribution are observed between 21 and 22 May and reflect changes in size distributions as well as aerosol chemistry. Further analysis of hygroscopic growth measurements and size-resolved chemistry during this period will provide additional insight to the role of aerosol mixing states and chemistry on CCN activity.

Comparisons of CCN concentrations (at 0.22% S_c) between the ground-based measurements at Cabauw and the airborne measurements on the SAFIRE ATR-42 indicate that CCN measurements on the ground often over-estimate the concentrations at levels where clouds form (Figure 4). During the clean background conditions when the air masses originate from the North Sea and cloud bases are relatively low, the boundary layer is well mixed and CCN concentrations at the ground resemble those at cloud base. The difference between ground-based and airborne measurements is especially important at higher concentrations associated with local pollution and when boundary layer mixing timescales are greater than...
the timescales for transport. In addition, multiple layers of aerosols with different origins related to long-range transport, especially during the Sahara dust episode, further complicate the relationship between in-situ ground-based and airborne CCN measurements. Lidar observations at Cabauw and on the ATR-42 detect the multiple aerosol layers as well as boundary layer mixing and are useful tools to investigate the relationships between ground-based and airborne measurements.

Figure 1. Times series of CCN measurements at the Cabauw supersite during EUCAARI-IMPACT. The color gradient show the supersaturation (%) of the CCN concentrations (color bar on right axis). The magenta stars show boundary layer CCN concentrations on the ATR-42 aircraft (at 0.22% SS). The red dots at the end of the time series are the comparison between the two CCN instruments installed at Cabauw (Table 1).

Figure 2. CCN spectra for each of the major sources of aerosols identified during the EUCAARI-IMPACT experiment.
Figure 3. Size distributions of aerosol particles (30 < \(d_p\) < 300 nm) and CCN at 0.15% and 0.43% \(S_c\). Note that data has not been corrected to actual concentrations.

Figure 4. Comparison of CCN concentrations (at 0.22% \(S_c\)) between the ground-based measurements at Cabauw and the airborne measurements on the ATR-42. The boundary layer data indicates measurements taken at the low end of the vertical profile. The cloud base data indicates measurements within a few hundred meters of cloud base. The concentrations at Cabauw are interpolated to yield concentrations at 0.22% \(S_c\).
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Retrieving satellite cloud properties for field experiments

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Keywords: Cloud microstructure, satellite retrievals

ABSTRACT

A major objective of EUCAARI is the understanding of effects of aerosols on clouds. The main effort of the HUJI has been to provide to the field campaigns with the regional context of cloud-aerosol interactions by using satellite reprieved fields of cloud properties and aerosols. The METEOSAT Second Generation (MSG) is particularly useful for that purpose, because it provides the possibility to retrieve cloud drop effective radius at a temporal resolution of 15 minutes and spatial resolution of about 5 km over Western Europe.

We have retrieved and provided the fields of cloud top effective radius ($r_e$), cloud top temperature (T) and other parameters using the MSG for the two field campaigns conducted so far. This was done for the observations over the Jungfrau Joch during February and March 2007, and for the field campaign over Cabauw during May 2008. We used the retrieval method described in Lensky and Rosenfeld (2008) and the references therein. The effective radius was retrieved using the 3.7 $\mu$m reflectance (as opposed to using 2.1 or 1.6 $\mu$m), to minimize 3-D and surface effects in these shallow clouds (Rosenfeld et al., 2004). We created satellite microphysical rendering for each MSG slot, using the method first described by Rosenfeld and Lensky (1988) and with the tool that they developed and described in Lensky and Rosenfeld (2008). An example is provided in Figure 1. The MODIS aerosol depth for that day is provided in Figure 2. This was done for 15 minute time slot during the daylight hours. In addition, a text table with the satellite retrieved parameters for all the grid points was provided for each time slot.

We are looking forward to the interactions with the people who analyze the results of the field campaigns for integrating our "synoptic microphysical view" with their specific measurements.
Figure 1. An Example of RGB microphysical rendering of the MTEOSAT Second Generation data during the Cabauw field campaign. The red is modulated by the visible solar reflectance, the blue is modulated by 10.8 \( \mu \text{m} \) brightness temperature, and the green is modulated by the 3.9 \( \mu \text{m} \) solar reflectance component. Greener means smaller cloud particles. The black frame enclosed the area of the field campaign, for which the physical values of the field of view are saved.
Figure 2. The MODIS aerosols optical depth for the case shown in Figure 1.

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TOWARDS THE PARAMETERIZATION OF AEROSOL INDIRECT EFFECTS IN THE LARGE SCALE MODELS

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Keywords: anthropogenic aerosol, boundary layer clouds, marine stratocumulus, diurnal cycle

INTRODUCTION

The idea that anthropogenic aerosol can alter the earth radiative budget via its multiple interactions with radiation and clouds is now widely recognized. Nevertheless, the complexity of these interactions renders the quantification of the aerosol effects on climate extremely problematic. As a fact, the sign and the amplitude of the radiative forcing induced by aerosol particles represents nowadays one of the main sources of uncertainty for the estimation of future climate changes (IPCC, 2007). It is therefore crucial to gain a better understanding of the aerosol effects and to include them in the numerical weather prediction (NWP) and the climate models.

Among the different ways in which aerosol particles can modify the earth radiative budget, their effects on cloud radiative properties and on precipitation efficiency, i.e. the indirect effects, are particularly controversial. One of the main reasons is that it is extremely difficult today to document such impacts from observations (Stevens and Brenguier, 2008; Brenguier and Wood, 2008; Sandu et al., 2008a). To illustrate this drawback, let’s consider the case of marine boundary layer clouds, typically marine stratocumulus, which are particularly sensitive to changes in the aerosol loading (Ackerman et al., 2004; Sandu et al., 2008a; Stevens and Brenguier, 2008). These low clouds, whose liquid water content is typically a few hundredths of the total water content, are in the same time extremely sensitive to very small changes of the thermodynamic state of the boundary layer. One should note that the variations of the heat and moisture budgets within the boundary layer which may lead to a doubling of the cloud thickness, or to its complete dissipation, are several orders of magnitude lower than the errors associated to the measure of these tendencies. Therefore, while observing two cloud systems characterized by different aerosol types, and hence having different histories, it is impossible to distinguish the impacts of aerosol on their evolution from the impacts caused by some extremely small, and non-measurable, variations of the large scale forcings. Only high resolution numerical models, i.e. widely known as Large Eddy Simulations (LES) models, allow to perform such experiments in which the large scale forcings are identical while the aerosol type changes. Indeed, as long as they include an adequate set of parameterizations, these models are able to reproduce the interactions and feedbacks between aerosol loading and the key processes controlling the cloud lifetime.

This study presents a strategy based on Large Eddy Simulations and on a synergy of modeling and observations, which should allow us to develop more physical parameterizations of the aerosol - cloud interactions and to include them in the NWP and climate models. We focus here on the boundary layer clouds, because, as we previously mentioned, they are particularly sensitive to changes in the aerosol loading. The context is favorable for this work because the aerosol begins to be now well represented in these large scale models. However, the existing cloud parameterizations are not able to represent the coupling between the aerosol and the cloud dynamics.
OUR STRATEGY

Large Eddy Simulations of pristine (low Cloud Droplet Number Concentration, or CDNC) and polluted (higher CDNC) boundary layer clouds will constitute the central point of our strategy aiming to account for the aerosol - cloud interactions in the large scale models. The idea is to first use the LES of pristine/polluted cloudy boundary layers to identify the key mechanisms and processes which control the response of the cloud to a change in the aerosol loading. Indeed, these 3D simulations allow to precisely simulate the couplings between the formation of precipitation, the radiative transfer and the cloud dynamics, and they hence allow to emphasize the mechanisms of impact of the aerosol loading on the cloudy boundary layer. The high resolution simulations confer moreover an excellent framework for the evaluation and the development of 1D parameterizations.

In a second step, we will therefore use 1D - 3D comparisons to evaluate in which measure 1D models of cloudy boundary layers are able to represent the mechanisms of impact of the aerosol loading on the cloud evolution. This analysis will help us identify the processes and the interactions that have to be (better) parameterized in NWP and GCM. Finally, we will develop (or improve) parameterizations of these processes, suited for the large scale models, via an aggregation of processes based on an extended and representative LES database.

In the meantime, this work will rely on a synergy of LES and observations. Such an approach is necessary because, taken separately, neither observations nor LES simulation are sufficient to quantify the aerosol indirect effects. Nevertheless, the analysis of 3D simulations emphasizes measurable signatures of the aerosol impacts on the cloud dynamics and therefore allows to optimize the procedures of sampling and data analysis during future field campaigns. In return, better constrained observations will help validate the signatures of aerosol impacts emphasized by the LES, and validate thus the utilization of these 3D simulations for the development of 1D parameterizations.

APPLICATION FOR MARINE STRATOCUMULUS

For instance, we have begun to successfully apply this strategy for compact decks of marine stratocumulus. Thus, we used 36 hours LES of pristine (precipitating) and polluted (non-precipitating) marine stratocumulus to investigate the impacts of the aerosol loading on the evolution of the Stratocumulus Topped Boundary Layer (STBL) (Sandu et al., 2008a).

These simulations showed that the diurnal cycle of marine stratocumulus is significantly modified if the increase of the aerosol, and hence of the CDNC, is sufficient to inhibit the formation of drizzle. The response of the system to this increase is however not monotonic (Fig. 1). Thus, during the first night of simulation, the LWP increases with increased CDNC loading, but this tendency

![Figure 1: Time evolution of the horizontal mean LWP (g m$^{-2}$) for a pristine (precipitating) (black) and for two polluted (non-precipitating) (dark and light grey) simulations.](image)
is reversed after 10 LT. Indeed, the two polluted clouds are getting constantly thinner than the pristine one during the last 26 hours of the simulation. It appears thus that the increased CDNC loading leads to a thinning of the cloud, and not to its thickening, like it is actually parameterized in the large scale models.

The analysis of these simulations emphasized the mechanisms of impact of the aerosol loading on the diurnal cycle. Thus, it appeared that the sedimentation of liquid water (cloud droplets + rain drops) diminishes the water content at cloud top and reduces thus the intensity of vertical turbulent motions within the upper part of the cloud layer. This further leads to a weakening of the cloud top entrainment. These simulations thus corroborate previous findings that the inhibition of the cloud droplet sedimentation and drizzle precipitation in polluted case leads to stronger entrainment rates, hence to a more pronounced growth of the boundary layer.

In the same time, precipitation affects the evolution of the STBL mixing state (Fig. 2). The evolution of the non-precipitating STBL corroborates the widespread image of the diurnal variation of such boundary layers, wherein the boundary layer is well-mixed during night, while it is decoupled during daytime. In the precipitating case, the evaporative cooling of rain drops under the cloud base affects this evolution, so that the STBL is decoupled during the night and it is less decoupled that the non-precipitating one during the day.

Moreover, we used the simulations of pristine/polluted STBLs to investigate weather simple models, such as a Mixed Layer Model (MLM), were able to reproduce the impact of the aerosol on the evolution of the STBL (Sandu et al., 2008b). This study emphasized that a model which is unable to represent the vertical structure of the STBL, and its modulation by precipitation, cannot reproduce the divergent evolutions of a precipitating and a non-precipitating cloud.

This work emphasized the processes on which we should focus on in order to reproduce the impacts of aerosol on the STBLs in large scale models. We make reference for example at the processes controlling the vertical structure of the cloud layer, i.e. the sedimentation of cloud droplets and rain drops, and of the STBL, i.e. the evaporation of precipitation and the radiative transfer. We also found that if the vertical structure would be correctly reproduced, the current parameterizations
of the surface fluxes would perform well. Moreover, some of the existing parameterizations for the entrainment rate perform quite well, though they should be revised to account for the dependence to CDNC.

Finally, the simulations of pristine and polluted diurnal cycles were equally used to identify measurable signatures of aerosol impacts on the cloud evolution and to make some suggestions for the experimental strategies of EUCAARI and VOCALS campaigns. It was thus showed that the differences between pristine and polluted STBLs consist in different vertical profiles of the cloud water content (non-adiabatic/adiabatic), an increase of the variance of the vertical velocity at the top of non-precipitating clouds, different cloud structures (closed/open cells), a more marked diurnal cycle for the non-precipitating clouds, and a different vertical structure of the STBL during morning periods (less decoupled in precipitating cases).

**FUTURE WORK**

In the future we will focus on the improvement and the development of 1D parameterizations of the processes that appeared to be essential for the representation of aerosol impacts on the STBL. Moreover, this strategy will be applied to the other types of boundary layer clouds. First, we will focus on marine boundary layer clouds, i.e. sparse stratocumulus and trade wind cumulus, because they represent a key component of the climate system. Then, we will extend this work to continental boundary layer clouds, i.e. stratocumulus and cumulus.

**ACKNOWLEDGMENTS**

One of the authors, Irina Sandu acknowledges Meteo-France support for her Ph.D and EUCAARI project support for her Post-Doc in the GMEI group of CNRM.

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Modeling aerosol surface chemistry and gas-particle interaction kinetics with K2-SURF: PAH oxidation

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Keywords: Aerosol modelling, aerosol-surface interactions, aerosol-surface reactions

INTRODUCTION

Atmospheric aerosols are ubiquitous in the atmosphere. They have the ability to impact cloud properties, radiative balance and provide surfaces for heterogeneous reactions. The uptake of gaseous species on aerosol surfaces impacts both the aerosol particles and the atmospheric budget of trace gases. These subsequent changes to the aerosol can in turn impact the aerosol chemical and physical properties. However, this uptake, as well as the impact on the aerosol, is not fully understood. This uncertainty is due not only to limited measurement data, but also a dearth of comprehensive and applicable modeling formalizations used for the analysis, interpretation and description of these heterogeneous processes. Without a common model framework, comparing and extrapolating experimental data is difficult. In this study, a novel kinetic surface model (K2-SURF) was used to describe the oxidation of a variety of polycyclic aromatic hydrocarbons (PAHs) [Ammann & Pöschl, 2007; Pöschl et al., 2007].

METHODS

Integrated into this consistent and universally applicable kinetic and thermodynamic process model are the concepts, terminologies and mathematical formalizations essential to the description of atmospherically relevant physicochemical processes involving organic and mixed organic-inorganic aerosols. Within this process model framework, a detailed master mechanism, simplified mechanism and parameterizations of atmospheric aerosol chemistry are being developed and integrated in analogy to existing mechanisms and parameterizations of atmospheric gas-phase chemistry.

One of the key aspects to this model is the defining of a clear distinction between various layers of the particle and surrounding gas phase as seen in Figure 1 for compound “Z_k.” The system can be described by six separate layers: gas phase, near-surface gas phase, sorption layer, quasi-static surface layer, near-surface bulk and bulk.

![Figure 1: Representation of resolution of particle and gas layers in the model.](image)

The processes occurring at each layer can be fully described using known fluxes and kinetic parameters. Using this system there is a clear separation of gas phase, gas-surface and surface bulk
transport and reactions. The compound described in Figure 1, compound “Z”, is semi-volatile and thus found in all layers. Its partitioning can be calculated using the various flux values (J) shown in Figure 1. By describing these layers unambiguously and precisely, the interactions of all species in the system can be appropriately modeled. However, such detail is not necessary for all systems and the model can easily be simplified.

In describing the oxidation of polycyclic aromatic hydrocarbons (PAHs), the focus was on the interactions between the sorption layer and quasi-static surface layer. The results from a variety of published experimental studies [Kahan et al., 2006; Kwamena et al., 2004; Pöschl et al., 2001] were analyzed and compared utilizing K2-SURF. The mean residence time and adsorption enthalpy were estimated for O3 at the surface of substrates, suggesting the chemisorption of O3 molecules or O atoms, respectively.

A summary of O3 uptake coefficients observed under different conditions is shown in Figure 2. The observed dependence on O3 concentration as well as on other competitively adsorbing gas phase species (NO2, H2O) will be described and explained with the kinetic double-layer surface model K2-SURF.

REFERENCES

Improved boundary layer parametrisation in climate model ECHAM5

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Keywords: planetary boundary layer, entrainment parametrisation, Global Climate Model

INTRODUCTION

Stratocumulus, considered sometimes as the vast “climate refrigerator” of the tropics and subtropics (Bretherton et al., 2004) are an important part of the huge uncertainty concerning the global warming by the end of the century as presented by the IPCC in 2007 (Solomon et al., 2007). Indeed, because of the different interplay between parametrisations and resolved processes in the different models, the sign and amplitude of the response of the low cloud cover to climate change are still unknown (Zhu et al., 2007). Moreover, stratocumuli are in general shallower than a grid box level and therefore difficult to resolve in a GCM, but are very important in terms of Earth’s radiation budget.

Accurate simulations of stratocumuli are also very important for aerosol-cloud interactions and the influence of anthropogenic aerosols on clouds and climate. Following Albrecht’s hypothesis (increased aerosol number would result in smaller droplets for the same liquid water content and these smaller droplets are less likely to grow to precipitation size drops, Albrecht (1989)), the lifetime and/or liquid water path of these clouds are expected to increase in polluted cases. But marine boundary-layer clouds polluted by aerosols are not necessarily observed to hold more water (Coakley and Walsh, 2002).

Recent nocturnal LES studies show that entrainment at the cloud-topped boundary layer is very important in regulating the cloud liquid water content in polluted conditions (Ackermann et al., 2004; Bretherton et al., 2007). Also more recently, Sandu et al. (2008) emphasized the reduction of the liquid water path (LWP) in polluted environment. This is due to the interaction entrainment - warming by solar radiation - drizzle evaporation - reduced sensible heat flux, their simulations even suggest this response to be irrespective to the large scale forcing. In the mean time, Hill et al. (2008) pointed out that ignoring the change in LWP due to evaporation-entrainment feedback associated with increasing CCN concentrations can result in a significant overestimation of the indirect forcing estimate.

The aim of this study is thus to implement an explicit entrainment parametrisation depending on the aerosol number and the diurnal forcing in our GCM \textit{ECHAM5} in order to study the interaction of aerosol-drizzle-entrainment in a warming climate.

For this study, we use the new version of the Hamburg general circulation model \textit{ECHAM5} coupled to the double moment modal aerosol microphysics scheme HAM (Stier et al., 2005). The cloud scheme in \textit{ECHAM5} that is used for this study includes the double-moment cloud microphysics scheme for cloud droplets and ice crystals (Lohmann et al., 2007).

PARAMETERIZATION OF TURBULENT DIFFUSION ON CONSERVED VARIABLES

Like in most others turbulent parametrisation scheme, the turbulent mixing is performed on dry variables (water vapor, liquid and ice mixing ratios, dry static energy) in the standard \textit{ECHAM5}
GCM. This will tend to vertically homogenized the cloud water, and then to destroy stratocumuli. The turbulent transport has been adapted to be done on conserved variables, the moist static energy and total water mixing ratio. This is already done in several GCM, for example in the Met Office GCM (Lock et al., 2000) or IFS (IFS documentation, 2006).

![Figure 1: Upper pannel, left: annual mean total cloud cover in the standard version [%] (STD). Upper pannel, right: annual mean total cloud cover in the version with reduced minimal width of PDF [%] (RED). Lower pannel: difference of the annual mean total cloud cover between the version with diffusion on conserved variables (MOIST) and RED.](image)

The tricky thing is then to retrieve the dry variables (vapour, liquid and ice mixing ratio, temperature) from the conserved diffused variables (total mixing ratio and moist static energy). In order to do it, the statistical cloud cover scheme Tompkins (2002) was used, where the minimal width of the total mixing ratio probability density function (PDF) has been reduced.

Figure 1 shows the annual mean cloud cover for the different versions. Indeed, as already mentioned, to retrieve the liquid mixing ratio accurately, the minimal width of the PDF in the model had to be reduced (RED); this minimal width is a tuning parameter (A. Tomkins, personal communication). This change implies a very big change in the global cloud coverage, meaning that this version would need a new tuning. On the other hand, looking at the difference between the version with diffusion on conserved variables (MOIST) and this RED version, the cloud coverage in all the stratocumulus regions has been significantly improved.
PARAMETERISATION OF EXPLICIT ENTRAINMENT AT CLOUD TOP

Based on conserved variables diffusion, different explicit entrainment parametrisations will be tested in *ECHAM5*: we start with the simple Turton and Nicholls (1987) entrainment closure. It is an extension of the dry convective boundary layer entrainment closure. It depends on the convective velocity (estimate of the overturning velocity in the large eddies) in the boundary layer, the boundary layer height, the buoyancy jump and an entrainment efficiency simulating the effect of evaporative cooling at the top of the boundary layer.

Results using this entrainment parametrisation will be presented at the EUCAARI meeting.

ACKNOWLEDGMENTS

This work was supported by the EU project EUCAARI.

REFERENCES


MODELLING THE TURBULENT MIXING AND ATMOSPHERIC PARTICLE FORMATION IN BOUNDARY LAYER WITH MALTE

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Keywords: atmospheric aerosols, modelling, turbulent mixing, boundary layer

INTRODUCTION

MALTE (Model to predict new Aerosol formation in the Lower Troposphere) is a 1-dimensional model that is designed to simulate aerosol formation and mixing in a vertical column of atmosphere (Boy et al., 2006). The leading idea of MALTE has been to include all essential phenomena that are related to new particle formation: aerosol dynamics, gas phase chemistry, and vertical mixing. A great advantage compared to 0-dimensional box models is, that in MALTE turbulent vertical mixing can be modelled. Still MALTE is computationally efficient enough to be used in detailed process modelling, which is not possible with 3-dimensional global or regional models.

Mixing between the atmospheric boundary layer (ABL) and the free atmosphere favours new particle formation as it leads to dilution of background aerosol concentration (e.g. Nilsson et al., 2001). In addition, e.g. temperature and thereby saturation ratio may differ significantly between the surface and the upper part of ABL. Therefore it has been speculated that nucleation may take place in the upper part of the boundary layer, where saturation ratio of e.g. sulphuric acid is higher due to lower temperature than close to the surface. MALTE offers a tool to investigate how vertical mixing and vertical profiles of different quantities affect the new particle formation.

RECENT IMPROVEMENTS TO MALTE

We have improved the representation of mixing in MALTE by implementing different mixing schemes: a turbulent kinetic energy closure model by Sogachev et al. (2002) and an asymmetric convective model by Pleim (2007). Pleim (2007) has combined the effects of local mixing and nonlocal large eddies, and the scheme is especially applicable to particle (and gas) flux simulations. These improvements enable more realistic studies of particle formation and mixing in the ABL.

To investigate the effect of the temperature profile on nucleation, we use a temperature dependent saturation vapour pressure for sulphuric acid, which has been previously treated in the model as totally non-volatile, i.e. with $p_{\text{sat}} = 0$.

As a case study, we present model simulations on days when measurements from a hot-air balloon were performed in Hyvtiilä, Finland, in springs 2006 and 2007 (Laakso et al., 2007). During balloon flights particle number concentration ($> 10$ nm) and ion concentrations in different size ranges were measured, as well as meteorological parameters such as temperature and relative humidity. We compare the simulated profiles of particle number concentration and ion concentrations across the boundary layer with the measured concentrations. We test different nucleation mechanisms (cluster activation nucleation, ion-induced nucleation and organic nucleation), and examine the relevant importance of these mechanisms and their ability to explain the observed particle and ion concentrations.
ACKNOWLEDGEMENTS

This work was supported by the Maj and Tor Nessling Foundation (Grant No. 2008310).

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VALIDATION OF MODIS AEROSOL ALGORITHM

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Keywords: aerosol measurements, satellite remote sensing, optical properties

INTRODUCTION

Atmospheric aerosols affect climate directly by scattering and absorbing the solar radiation and indirectly by modifying radiative properties, amount and lifetime of clouds. Radiative forcing by anthropogenic aerosols is estimated to be of the same order of magnitude, but opposite of sign, as radiative forcing by the anthropogenic greenhouse gases (IPCC, 2007).

As compared to greenhouse gases, aerosols have shorter lifetime, from several days to several weeks, and, hence, their concentrations in the atmosphere are variable. Because of the spatial and temporal variability, the uncertainty of estimating human-induced aerosol forcing on climate remains dominant in global climate modeling (Remer et al, 2004, IPCC, 2007). Only satellite remote sensing can achieve the global coverage and the necessary spatial resolution to measure inhomogeneous aerosol fields. Satellite remote sensing of aerosol optical properties is best possible over surfaces with a low and preferably constant albedo. Most land surfaces have high surface reflectivity, which makes satellite remote sensing extremely difficult. On the other hand, the albedo of the ocean is low and relatively well known. (Veefkind and de Leeuw, 1998). For this reason, algorithms retrieving aerosol properties over ocean give better results than ones over land.

There exist discrepancies between retrievals of aerosol properties, even over ocean regions. Comparisons of these satellite aerosol retrievals with the surface observations provide an opportunity to both evaluate and improve the accuracy of these satellite retrievals (IPCC, 2007).

The aim of our work is to evaluate aerosol optical properties retrieved from observations of MODIS (Moderate Resolution Imaging Spectroradiometer) sensors on the board of NASA’s Terra and Aqua satellites. Retrievals of collection 5 are used for this purpose.

In the future we plan to validate and intercompare results from other sensors. They include MERIS (MEdium Resolution Imaging Spectrometer) and AATSR (Advanced Along Track Scanning Radiometer) on board the European satellite ENVISAT and POLDER (Polarization and Directionality of the Earth’s Reflectance) on board French microsatellite PARASOL.

METHODS

MODIS aboard Aqua and Terra satellites is designed to characterize atmospheric aerosols. The aerosol product derived from MODIS observations now includes a 7 year record from Terra-MODIS and a 5 year record from Aqua-MODIS. The MODIS aerosol algorithm consists actually of three independent algorithms, two to derive aerosol characteristics over land, and the third for application over ocean. This work is restricted to using results over ocean. The MODIS product includes retrievals of aerosol optical depth (AOD) at seven wavelengths over ocean (470 nm, 550 nm, 660 nm, 870 nm, 1240 nm).
nm, 1630 nm and 2130 nm) (Remer at al., 2008). In our work we’ll consider AOD and Angstrom coefficient.

For evaluation of these data we use measurements from NASA’s AERONET (Aerosol Robotic NETwork, Holben et al., 1998) stations. This network consists of hundreds of automatic instruments that measure AOD to within 0.01 accuracy and retrieve other aerosol characteristics (Remer et al., 2008). AERONET sun photometers derive AOD at wavelengths of 0.34, 0.38, 0.44, 0.50, 0.67, 0.87, and 1.02 μm from direct solar radiation measurements (Ichoku et al., 2002). Then these measurements are interpolated to MODIS wavelengths. In this work we used measurements of AOD from 23 AERONET stations, which are situated on islands or at coastal areas. A map displaying locations of these stations is shown on the Figure 1.

![Figure 1. Map showing locations of AERONET stations used for the evaluation of aerosol optical properties over ocean retrieved from MODIS observations.](image)

RESULTS

First results show strong correlation (correlation coefficients are 0.90 – 0.94) between surface-based and satellite measurements for all 7 wavelengths considered (see Figure 2). The example picture shows comparison of AOD between MODIS and AERONET data for 550nm wavelength. AOD retrieved from Terra showed a little better correlation than one from Aqua.
CONCLUSION

The work presented is a preliminary result on the intercomparison of AOD from several satellites, including MODIS, MERIS and AATSR, over ocean. The next step is to evaluate results obtained from the simultaneous use of AATSR and MERIS, an algorithm for which is currently developed.

REFERENCES


NEW PARTICLE FORMATION AND AEROSOL PARTICLE CHARACTERISTICS IN A SEMI-CLEAN SAVANNA ENVIRONMENT

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Keywords: new particle formation, air pollution, Southern Africa, savannah, Modis, Hysplit.

INTRODUCTION

Air quality and interactions between land ecosystems and atmosphere in a changing climate are issues that influence most of the developing world. In Africa, for example, changing climate affect vegetation and may thereby cause emigration (Boko et al., 2007). Emigration, on the other hand, increase urban population and air pollution. Although most of the population accumulates into urban areas, air quality is affected also by the surrounding landscape, and, with respect to air quality, Africa is one of the least studied continents in the World (Laakso et al., 2006).

Despite some previous observations, in Africa combined long-term measurements of trace gas concentrations, aerosol particle mass concentrations and number size distributions (especially in ultrafine size range), air ion number size distributions and meteorological variables are practically non-existent. Also the exposure of people to air pollutants in informal settlements, heavily-industrialized areas and mining regions is poorly known (Piketh et al., 2005; Laakso et al., 2008).

In order to get a more detailed picture on various aerosol and related trace gas properties in various environments in southern Africa, we built a transportable measurement trailer (Petäjä et al., 2007). The background measurements for 1.5 years in Botsalano game reserve have now been completed and in this abstract we will describe some preliminary results of a relatively clean savannah environment from the period 20 July 2006 to 30 January 2008.

METHODS

The measurements in the trailer include aerosol particle size distribution from 10 to 840 nm using a DMPS system with time resolution of 7.5 minutes, air ions and charged particles from 0.4 to 40 nm using a Air Ion Spectrometer (AIS, Airel Ltd, Estonia, Mirme et al.2007), aerosol mass concentration using Tapered Element Oscillating Microbalance (TEOM) model 1400a (Rupprech and Patashnick R&P, Co. Inc.) and trace gases (SO₂, NOₓ, CO and O₃). For a more detailed discussion on the technical details of the trailer and the measurements see Petäjä et al. (2007) and Laakso et al. (2008).

In addition to the measurements in the trailer 96-hour back-trajectories were calculated for each hour during the measurement period using HYSPLIT 4.8 model (Draxler and Hess, 2004). Trajectories were calculated on three arrival heights of 70, 100 and 300 m. We used the GDAS global meteorological archive (http://www.arl.noaa.gov/archives.php), which has a one degree latitude longitude resolution.

Satellite information on biomass burning was obtained from MODIS Thermal anomalies product (Kaufman et al., 2003) and it was combined with back-trajectories to further analyse the effect of fires.

A one to three-modal log-normal size distribution was fitted on the aerosol particle size spectra from the DMPS system for the whole measurement period. For a description on the fitting method used see...
Vartiainen et al. (2007). New particle formation events were classified and formation and growth rates calculated according to Dal Maso et al. (2005). From the ion spectra the growth rates for 1.5-3nm, 3-7nm and 7-20nm ions were calculated using the method described in Hirsikko et al. (2005). The 2-3nm ion formation rate $J_2^\pm$ was calculated as

$$J_2^\pm = \frac{dN_2^\pm}{dt} + CoagS_{2-3} \cdot N_2^\pm + \frac{GR}{3nm-2nm} \cdot N_2^\pm + \alpha \cdot N_2^\pm \cdot N_{<3nm}^- - \beta \cdot N \cdot N_{<3nm}^\pm,$$

where $N_2^\pm$ refers to ion 2-3nm concentration, $N$ to the concentration of neutral 2-3nm particles, $CoagS_{2-3}$ coagulations sink for 2-3 nm particles, $GR$ growth rate, $\alpha$ ion-ion recombination coefficient and $\beta$ ion-aerosol recombination coefficient (Kulmala et al. 2007). For the calculation of ion $J_2$ we assumed $N$ to be twice the sum of the total 2-3nm ion concentration.

**RESULTS**

The average particle growth rate for particle size range 10-30 nm was 9.2 nm h$^{-1}$ and average formation rate of 10nm particles, $J_{10}$, 4.7 cm$^{-3}$ s$^{-1}$ (Figure 1).

The average ion (or charged particle) growth rates for size ranges 1.5-3 nm, 3-7 nm and 7-20 nm were 7.6 nm h$^{-1}$, 10.1 nm h$^{-1}$, and 8.6 nm h$^{-1}$, respectively. The average ion $J_2$ was 0.3 cm$^{-3}$ s$^{-1}$ (Figure 2).

Both DMPS and AIS growth rates show a weak minimum during winter and maximum at spring and summer, as do observations from other sites (Kulmala et al., 2004). The levels of growth rates and formation rates are among the highest observed in continental areas (Kulmala et al., 2004; Hamed et al., 2007).

Figure 1 Monthly averaged 10-30nm growth rate and 10nm formation rate from DMPS data. November GR is based on only two well-behaving nucleation events due to poor data coverage in November 2006 and 2007.
Figure 2 Monthly averaged growth and formation rates for ions on different size ranges. Data from March-April 2007 is missing as the device was under maintenance in Estonia.

The diurnal behaviour of the log-normal distribution fitted in the DMPS data is presented in Figure 3. The strong and frequent new particle formation during morning hours is clearly visible in the increase of the nucleation mode particle number.

Figure 3 Average fitted modal parameters, diurnal behaviour.

An example on the MODIS fire data combined to back-trajectories for a single day (1 October 2006) is given in Figure 4. For this day, the average DMPS total concentration for trajectories passing by fires closer than 20km was 1600 cm$^{-3}$ but for trajectories passing fires further than 20km the average concentration was 900 cm$^{-3}$. 

222
CONCLUSIONS

The observed formation and growth rates, as well as the new particle formation frequency, are among the highest reported in the literature, and thus the particle formation may significantly modulate the clouds and their properties. The effect of wild fires was also preliminary investigated for few example days and a new MATLAB-based tool, suitable for use on all EUCAARI-stations combining MODIS fire data, HYSPLIT trajectories and field observations was developed.

REFERENCES


Atmospheric aerosol particles can act as cloud condensation nuclei (CCN) and eventually form clouds. These clouds affect the radiative balance of the atmosphere by scattering and absorbing light. This is called the indirect effect of atmospheric aerosols, and can be either cooling or warming. It is one of the least understood processes affecting climate change (IPCC, 2007). The ability of an aerosol particle to act as a cloud condensation nucleus depends mainly on the size of the particle (Dusek et al., 2006), but chemistry also plays a part by affecting the hygroscopicity of the particle. In this study measurements of CCN concentrations at the SMEAR II station in Hyytiälä, Finland are evaluated and compared to hygroscopicity measurements from a hygroscopicity tandem differential mobility analyzer (HTDMA).

**METHODS**

CCN concentrations were measured with a commercial diffusion-type CCN counter (Droplet Measurements Technologies inc.) (Roberts and Nenes, 2005). The sample flow surrounded by sheath flow (1/10 flow ratio) is led through a vertical column with walls wetted by water. The column temperature increases along the flow, generating a stable supersaturation. The particles that activate and grow by condensation will be detected by an optical particle counter. The concentration of the cloud condensation nuclei is obtained as a function of the supersaturation. Supersaturations of 0.1, 0.2, 0.4, 0.6 and 1.0 % were used. The CCN counter was calibrated by using ammonium sulphate particles.

The activation of an aerosol particle into a cloud droplet is described by the Köhler equation (Köhler 1936):

$$S = \gamma_w x_w \exp\left(\frac{4M_w \sigma}{RT \rho D_p}\right),$$  

where $S$ is the saturation ratio, $\gamma_w$ is the activity coefficient, $x_w$ is the mole fraction of water, $M_w$ is the molar mass of water, $\sigma$ is the surface tension of the solution, $R$ is the universal gas constant, $T$ is temperature, $\rho$ is the density of the solution and $D_p$ is the diameter of the initial dry particle. Atmospheric aerosol particles often have insoluble cores, and for this situation the Köhler equation is described by Laaksonen et al. 1998.

The total aerosol particle size distribution is measured by using a differential mobility particle sizer (DMPS) (Aalto et al. 2001). By comparing the CCN concentration and total particle concentration, the activated fraction is achieved. The DMPS data can also be used to calculate an approximation for the critical particle diameter for all the supersaturations used. In order to obtain this, the activation probability is assumed to behave like a step function, with all particles above the critical size activating. The particle size distribution is summed from the largest particle sizes towards the smallest sizes until the CCN concentration is obtained. At that point the diameter corresponds to the critical diameter.
A HTDMA (Ehn et al., 2007) was used to measure the hygroscopicity of aerosol particles. In this instrument, sample aerosol is first brought through a drier and a radioactive charger in order to reach charge equilibrium and a relative humidity below 20%. After this a certain dry particle size, $D_{\text{dry}}$, is selected using a differential mobility analyzer (DMA). Next the particles are passed through a humidifier so that a certain controlled relative humidity is reached. Finally the humidified aerosol passes through another DMA which is used as a DMPS. Thus a humidified size distribution for a certain $D_{\text{dry}}$ is measured. The second DMA was located in a temperature controlled box, maintained at a temperature of 19ºC and relative humidity of 90%. Four dry sizes (110nm, 75nm, 50nm and 35nm) were used which belong to the standard sizes agreed inside the EUCAARI project. The hygroscopicity of a certain dry size can simply be described as a growth factor

$$g_a = \frac{D_{\text{wet}}}{D_{\text{dry}}},$$

(2)

where $D_{\text{wet}}$ is a mean diameter calculated from the humidified size distribution for a certain $D_{\text{dry}}$. The soluble fractions for different dry sizes were calculated using the equation

$$\varepsilon = \frac{V_{\text{sol}}}{V_{\text{tot}}} = \frac{g_{\text{sol}}^3 - 1}{g_{\text{tot}}^3 - 1},$$

(3)

(Swietlicki et al., 1999). Here $g_{\text{sol}}$ is the known growth factor of the fully soluble reference substance with the same humid particle size as the ambient particle ($D_{\text{wet}}$). In this study ammonium sulphate was used as a reference and ambient aerosol was simply assumed to be a mixture of insoluble material and ammonium sulphate. In most cases the ambient aerosol is a much more complex mixture of different soluble and insoluble compounds. Nevertheless this approach is widely used in HTDMA studies and can provide comparable information when there is no definite knowledge about the chemical composition of the aerosol.

RESULTS AND CONCLUSIONS

In figure 1 the critical diameter, calculated from the CCN data, is presented as a function of supersaturation, together with the corresponding critical diameters of the pure ammonium sulphate particles. The critical diameters for the measured aerosol are larger than for ammonium sulphate, most likely due to insoluble or slightly soluble compounds mixed in the particles. The insoluble fraction can be calculated by assuming that particles contain only an insoluble compound and ammonium sulphate. We obtained the insoluble fraction by iterating the insoluble fraction in the Köhler equation by Laaksonen et al. 1998 to fit the measured data. The results are shown in the figure 2. Also the insoluble fractions calculated from the HTDMA data $(1-\varepsilon)$ are shown in the figure. Soluble fractions $\varepsilon$ obtained from the HTDMA data are in agreement with previous results for the boreal forest aerosol (Hämeri et al., 2001). The Aitken mode ($<100$ nm) can be seen to differ from the accumulation mode ($>100$ nm) for both HTDMA and CCNC data even though the absolute values obtained with these two methods do not agree. In the Aitken mode the soluble fraction seems to get larger towards smaller sizes according to the HTDMA results which is not seen in the CCNC results. This is reasonable since smaller sizes are more affected by the nucleation mode particles which have been shown to have relatively high soluble fractions during nucleation events (Hämeri et al., 2001). There are several possible error sources which may have lead to the difference between the two approaches mentioned above. In these early considerations only a visual evaluation was used to select which days to use and all calculations were done for the average values. Furthermore, instead of measured ammonium sulphate calibrations, theoretical values for the $g_{\text{sol}}$ were used. As the data analysis continues, many of the error sources will be eliminated.
Figure 1. Critical diameter from the CCNC data and for ammonium sulphate particles as a function of the supersaturation.

Figure 2. Insoluble fraction as a function of particle diameter calculated from CCNC and HTDMA data.

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Aerosol Direct Radiative Effect from OMI: Concept and First Result

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Keywords: aerosol, absorption, direct radiative effect, closure experiment.

INTRODUCTION

In the present study it is shown for a well characterized test case that the shortwave direct radiative effect of aerosols can be estimated using OMI reflectance measurements. In the framework of the EUCAARI Intensive Observation Phase (IOP) in May 2008 numerous ground-based, air-borne and in-situ measurements have been performed in order to study cloud and aerosol interactions at Cabauw in the Netherlands. The test case used in the present study is characterized by the IOP measurements at noon on 10 May 2008. Radiative transfer simulations are performed to describe the radiation field in this test case using aerosol optical thickness $\tau$ and single scattering albedo $\omega$ data from ground-based sun-photometer measurements (AERONET); atmospheric profile data are taken from radiosonde measurements. The simulated broad-band radiative fluxes agree excellently with ground-based pyranometer and pyrheliometer measurements. The simulated radiation fields with and without aerosols are used as a reference for radiative effect estimates from OMI.

CONCEPT

OMI-Aura (Ozone Monitoring Instrument) is primarily designed to measure ozone but is also sensitive to aerosol [Torres et al., 2002; Veihelmann et al., 2007]. The multi-wavelength algorithm (OMAERO product) uses OMI reflectance measurements in 14 wavelength bands located between 342.5 and 483.5 nm. In this algorithm the aerosol optical thickness $\tau$ is retrieved for a number of aerosol models and a best fitting aerosol model is selected. In a prototype version of the multi-wavelength algorithm the albedo at the top of the atmosphere $a_{\text{TOA}}$ associated with these aerosol models is calculated viz.:

$$a_{\text{TOA}} = a_{\text{path}} + \frac{a_{\text{surf}} T}{1 - a_{\text{surf}} S}$$

The albedo for a black surface $a_{\text{path}}$, the transmission term $T$, and the spherical albedo of the atmosphere for illumination from below $S$, have been pre-calculated with the Doubling Adding Code KNMI (DAK) for each aerosol model and a range of aerosol optical thickness values. Note that directional reflectance at the top of the atmosphere is parameterized in a similar way in the operational multi-wavelength algorithm. The upwelling radiative flux at the top of the atmosphere $F_{\text{TOA}}$ is obtained by integrating the product of the monochromatic albedo $a_{\text{TOA}}(\lambda)$ with the solar spectrum $s(\lambda)$ viz.:

$$F_{\text{TOA}} = \int a_{\text{TOA}}(\lambda) \ s(\lambda) \ d\lambda$$

This parameterization allows efficient flux calculations for a model atmosphere that is associated with an aerosol model. The flux $F_{\text{TOA}}$ is evaluated for the best fitting aerosol model and the aerosol optical thickness that has been retrieved from an OMI measurement and also for an optical thickness of zero. The direct radiative effect at the top of the atmosphere is defined as the resulting flux difference such that negative values indicate a cooling effect. Currently the radiative flux is calculated for a wavelength range from 362 nm to 452 nm. It is envisaged to extrapolate the flux calculations to wavelengths up to 700 nm.
RESULT

The flux based on the OMI measurements agrees very well with the flux based on IOP measurements (30 W/m² in the range from 362 nm to 452 nm). This holds for the flux from OMI measurements of the nearest ground pixel and also for the average flux from OMI measurements within a 50 km radius centred at Cabauw (see Table 1). Good agreement has been found for estimates of the direct radiative effect based on the IOP measurements and estimates based on OMI measurements of the nearest ground pixel (-3.6 W/m²). The direct radiative effect based on OMI measurements within a 50 km radius deviates by ~1.5 W/m² from the reference. The aerosol retrieval and the flux calculations based on OMI measurements have been performed assuming the surface albedo spectrum that has been used in the flux calculations based on the IOP data. The operational multi-wavelength algorithm uses a surface albedo climatology. Therefore, the aerosol retrieval and the flux calculations based on OMI measurements have been repeated assuming the surface albedo spectrum from the climatology. This influences the estimate of the direct radiative effect (2.2 W/m²) but has no significant impact on the flux calculation.

Table 1. Flux and direct radiative effect (DRE) estimates from IOP data and from OMI measurements.

<table>
<thead>
<tr>
<th></th>
<th>IOP Cabauw site</th>
<th>OMI Nearest pixel</th>
<th>OMI average 50 km radius</th>
<th>OMI average 50 km radius from climatology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Albedo</td>
<td>IOP</td>
<td>IOP</td>
<td>IOP from climatology</td>
<td></td>
</tr>
<tr>
<td>Flux TOA W/m²</td>
<td>30.4</td>
<td>29.7</td>
<td>31.1</td>
<td>30.1</td>
</tr>
<tr>
<td>DRE TOA W/m²</td>
<td>-3.6</td>
<td>-3.6</td>
<td>-5.0</td>
<td>-2.2</td>
</tr>
<tr>
<td>AOT at 483.5 nm</td>
<td>0.2</td>
<td>0.2</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Vertical dist.</td>
<td>0-1 km</td>
<td>0-2 km</td>
<td>0-2 km</td>
<td>0-2 km</td>
</tr>
<tr>
<td>SSA at 483.5 nm</td>
<td>0.89</td>
<td>0.95</td>
<td>0.95-0.97</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The results obtained thus far are valid for one specific location and time where the aerosol load is dominated by weakly absorbing aerosol types. It is envisaged to extend this study and to validate estimates for flux and radiative effect in various conditions including cases when absorbing aerosol types are present. It is assumed that the largest error source for direct radiative effect estimates is undetected cloud contamination. Using cloud masks from other sensors such as MODIS may reduce such errors efficiently.

REFERENCES


The role of tropospheric aerosol in climate has become a key issue in evaluating current and future climate change. Uncertainties in anthropogenic perturbations of direct scattering and indirect cloud effects dominate overall uncertainty in estimates of radiative forcing (IPCC, 2007). At the same time, epidemiological correlations of fine particle loading with adverse health effects are stronger than any other measure of air pollution (Docherty et al., 1994). Despite this interest, basic questions remain concerning the chemical budgets of ambient aerosol, particularly concerning the “organic” (carbonaceous) fraction. This follows multiple reports of unexpected large production of secondary organic aerosol in anthropogenically influence urban/regional outflow (DeGouw et al., 2005; Volkamer et al., 2006).

This paper will present measurements of sub micron aerosol composition using aerosol mass spectrometry, summarizing results from about 40 field campaigns (Zhang et al., 2007) as well as laboratory chamber results (). This includes comparisons of inorganic and organic composition, resolution of primary and secondary chemistry, and evolution (and growth) of aerosol size. We present a comprehensive picture of urban, regional and remote aerosol size and chemistry that can serve as the basis for evaluating global models of aerosol loading in the troposphere.

METHODS

The Aerodyne aerosol mass spectrometer (AMS) is now in routine use in many research groups throughout the world (Canagaratna et al., 2007). The instrument is a molecular beam mass spectrometer that utilizes an aerodynamic lens to focus sub-micron particles into a beam in vacuum. Particles impact a tungsten oven, typically heated to 600°C, vaporizing non-refractive inorganic and organic components which are then ionized using electron impact (EI) ionization followed by positive ion mass spectral detection. Aerodynamic particle size is determined by measuring particle time-of-flight between a rotating slit chopper wheel (100Hz) and the mass spectrometer. EI provides universal, quantitative detection of all vapor species produced at the oven.

It is straightforward to separate inorganic (e.g. SO4, NO3, NH4) and organic components in the resulting mass spectrum. The challenge is to classify the complex organic mass spectrum, which precludes molecular identification. Factorization has distinguished classes of primary and secondary organic composition (Zhang et al., 2005b; Lanz et al., 2007; Ullbrich et al., 2008). Recently a high resolution time-of-flight mass spectrometer has enabled elemental analysis of the inorganic and organic ions (Decarlo et al; Aiken et al). In summary, the AMS provides a unique, size resolved signature of the total non-refractory inorganic and organic sub-micron aerosol composition. In particular, vaporization at 600°C effectively detects all organic components, even highly oxidized (secondary) components, though refractory oxide (dust) and graphitic (black) components are not detected.

Fig. 1 shows the correlation of two organic components, HOA (hydrocarbon organic aerosol) and OOA (oxygenated organic aerosol), with CO and Ox (O3 + NO2) from a mountain measuring the outflow from
Mexico City (Herndon et al., 2008). The tight correlation of HOA with CO, which is largely independent of time of day and subsequent regional transport, is indicative of primary emission from vehicles (Zhang et al., 2005a), while the correlation of OOA with Ox is consistent with photochemical production of secondary organic aerosol. Such correlations have been observed in many locations, clearly showing the emission of primary organics in urban areas and the evolution of photochemically produces secondary organic in regional outflow and transport.

![Figure 1. HOA and OOA correlation with CO and Ox in Mexico City (Herndon et al., 2008). Note biomass burning plume which deviates from OOA-Ox correlation.](image)

These two organic aerosol types span aerosol health and climate impacts. HOA, which is associated with soot particles (Canagaratna et al., 2006; Slowik et al., 2006), is important in urban canter, particularly in morning “rush hour” conditions, where human exposure are highest, while OOA dominates global aerosol composition, particularly at remote and upper altitudes. Even in urban canters, OOA is larger organic fraction especially in summer (Zhang et al., 2005a), though not quite so much in winter (Weimer et al., 2006). More detailed factor analysis has identified OOA components that correlate well with nitrate and sulphate aerosol, indicative of relatively “high” and “low” volatility fractions (Lanz et al., 2007; Ullbirch et al., 2008). In general, the O:C ratio of secondary OOA varies between ~0.3 and 1.0, indicative of photochemical production of highly oxidized secondary organics.

REFERENCES


INTRODUCTION

In the month of May 2008 the EUCAARI-IMPACT campaign was held near the CESAR site at Cabauw, the Netherlands. The IMPACT campaign consisted of two major components, namely a ground based measurement campaign and an aircraft observation campaign designed to observe clouds and aerosols. This enabled a detailed investigation of the aerosol indirect effect. The CESAR site normally has large number of (active) remote sensing instruments and in-situ measurements at the site for the observation of clouds, aerosols, and radiation. The set of instruments, in particular for aerosol detection, was enhanced for the campaign by a large number of additional instruments from research groups from all over Europe. The new RIVM Raman lidar was used for the first time at the start of the campaign, giving high resolution aerosol and water vapor profile information. Also a new enhanced Leosphere wind cube for the detection of vertical wind speeds was implemented. The biggest advances were made in the area of aerosol measurements. Early in 2008 an aerosol pipe was added to the tower in order to ingest air at 60 meter and distribute it to multiple in-situ instruments in the basement of the laboratory. During the campaign up to 12 instruments were able to sample the exact same airflow resulting in a unique dataset.

The aircraft involved with the IMPACT campaign were

1. SAFIRE-ATR42 stationed at Zestienhoven (Rotterdam airport in the Netherlands)
2. IFT-ACTOS (helicopter) stationed next to the Cabauw site
3. NERC-Do226 stationed at Oxford.

Additionally there were a number of flights performed by the Wageningen University SkyARROW within the Dutch boarders in the month of May. This aircraft measures turbulence fluxes.

The ATR42 was the main aircraft during the IMPACT campaign, responsible for observations of the optical, physical, chemical and hygroscopic properties of aerosols (CN and CCN), cloud microphysics (warm clouds) and aerosol and cloud radiative properties. 20 scientific flights were executed during the entire month of May with around 60 hours of total flight time.

The helicopter team with the ACTOS sampled the atmosphere within 5 Nm from Cabauw to collect aerosol, cloud and radiation measurements during 12 scientific flights. Due to ATC regulations the helicopter was not allowed to rise above 6000 ft, except for 1 day. The high temperatures in May gave rise to relatively high cloud levels with cloud top often above 6000ft. This resulted in only one true cloud flight, where the probe could enter the cloud while flying above well developed Cu. One flight recorded the development of baby cumulus. All other flights were classified as aerosol flights. The helicopter measurements uniquely fill the gap between the single point measurements made at Cabauw and the horizontally more extensive flight tracks by the ATR42, in particular when the latter flew within the atmospheric box close to Cabauw.

The NERC Dornier performed five flights, concentrating solely on high resolution radiation measurements including polarization. The data are intended for radiation closure studies, clear sky cases (May 11th) as well as (scattered) cloud cases (other flights). Due to the prominently easterly winds in the first half of the month a large number of LONGREX flights past by in the vicinity of Cabauw.

CAMPAIGN

The month of May 2008 was atypical climatologically, with a mean of 15.7 °C versus a normal of 12.7 °C. As a result it was the warmest May month in over a century. According to climatology the wind direction in this month is from the south west resulting in relatively pristine aerosol loading. Due to a long period of high pressure systems north of the Netherlands the predominant wind direction was easterly resulting in a long period of clear sky days (May 4th -12th) in which the aerosol loading was relatively high, ideal for studies of the direct aerosol effect and aerosol closure studies. Due to the high temperatures cloud base was relatively high during the month; this especially hampered the study of these clouds by use of the helicopter platform.
In Figure 1 an overview of the daily short wave (sw) flux measurements is shown, including both the global and direct sw fluxes. When the two lines significantly differ, it indicates the occurrence of clouds. The clear sky period is prominently shown, as well as the high cloud cover in the last week. The third week shows nice signs of scattered cloud fields.

The goal of the campaign is to understand clouds, aerosols and their interaction. In Figure 1 a proxy for cloud occurrence is presented. In Figure 2 a similar overview is given for the aerosol loading during this month. Figure 2 present the CCN concentrations at 60 m, measured through the aerosol pipe. The measured concentrations reflect a combination of wind directions, and thereby the sources, and precipitation scavenging. These two figures only give a flavor of the type of days which occurred during the entire month. What is clear is that there were roughly three different regimes (clear sky with high aerosol loadings, northerly flow with low aerosol loadings (with Cu) and easterly flow with high aerosol loadings and clouds). The amount of data observed at the ground and in the air is enormous for all three periods and should enable many detailed research efforts for the coming years.

Figure 1: SW radiation measured at Cabauw (F. Bosveld) for all the days in May 2008. The red line denotes the direct flux, the green lines the observed global flux. When the red and green differ substantially it indicates the presence of clouds. Note the May 4th-12th cloud free period.

Figure 2: CCN concentrations measured at 60 m (G. Roberts) at different super saturations. The measured concentrations show very nicely the main atmospheric conditions (9-14th and 22-27th Aerosol origins from Central and Eastern Europe, 17-20th aerosols origins from the North Sea combined with precipitation scavenging. May 30th Long-range transport of Sahara dust in frontal system.
RESEARCH DIRECTIONS

In October a workshop to discuss for the first time the observations performed during the IMPACT campaign led to a list of different topics of scientific research for the coming two years. This idea was adopted to enhance the speed in which the different topics can be explored. It also provides an open list of people involved in the different topics and gives the opportunity for people to gravitate towards research groups of joint / similar interest. In principle anyone can contact the leaders of the major groups or directly contact the first name for a specific field when he or she feels a contribution can be made. When enlisted within one of the groups it is considered ‘polite’ to indicate to the coordinator if no effort can or will be made to actively engage within the research, e.g. when the assigned researcher leaves the group or has a higher priority task.

1. IMPACT overview (Reinout Boers: reinout.boers@knmi.nl)
   Overview of the experiment with a cursory survey of aims, synoptics, flights and initial data

2. Aerosol nucleation (Birgit Wehner: birgit@tropos.de)
   - Birgit Wehner + Arnoud Apituley(Arnoud.Apituley@rivm.nl): nucleation at elevated height
   - Bas Henzing (bas.henzing@tno.nl) + Uhel: nucleation at surface

3. CCN CDNC Closure (G. Roberts: gcrroberts@ucsd.edu)
   - Rupert Holzinger (r.holzinger@phys.uu.nl): compare CCN and aerosol number densities with PTR aerosol measurements Inputs from G. Roberts [CNRM]
   - Astrid Kiendler Scharr (a.kiendler-scharr@fz-juelich.de): link aerosol composition to CCN properties. Inputs on aerosol microphysics and CCN properties including hygroscopic.
   - Greg Roberts: CCN closure and coupling to clouds. Inputs on aerosol chemical and microphysics properties.
   - Sylvester Arabas (slyoyo@igf.fuw.edu.pl): CCN to droplet conc. Inputs on CCN properties and vertical velocity statistics from ground remote sensing (Herman Russchenberg [TU-Delft], Henk Klein Baltink [KNMI] and Matthieu Boquet/ J.P Cariou [Leosphere]), tower and aircraft.
   - Gerrit de Leeuw (gerrit.leeuw@fmi.fi): From HTDMA at Cabauw provide aerosol hygroscopic properties, inputs from TNO aerosol microphysics and chemical composition
   - Herman Russchenberg (H.W.J.Russchenberg@irctr.tudelft.nl): Aerosol, CCN and retrieval of CDNC from lidar/radar
   - Alfons Schwarzenboeck(a.schwarzenboeck@opgc.univ-bpclermont.fr): Aerosol chemical and microphysical properties on board ATR-42

4. Radiation closure (Gerrit de Leeuw: gerrit.leeuw@fmi.fi)
   - René Preusker (rene.preusker@wwu-berlin.de) + Damien Josset: column closure on clouds.
   - Wouter Knap (knap@knmi.nl) + FUB PhD + Gerrit de Leeuw + Damien Josset + Arnoud Apituley: clear sky column closure on aerosol
   - Frank Heinrich (henrichf@students.uni-mainz.de) + IFT: 3D heterogeneous bias
   - Hünnerbein : retrieval of LWP diurnal evolution from SEVIRI

5. LES (Thijs Heus: heus@knmi.nl)
   - Thijs Heus: Synergy between LES and observations
   - Stefan Horn (stefan.horn@tropos.de): validate the ASAM LES
   - Hanna Pawlowska (hanna.pawlowska@igf.fuw.edu.pl): Impact of entrainment-mixing on cloud radiative properties
   - Irina Sandu (irina.sandu@cnrm.meteo.fr): detect signatures of the aerosol impact on cloud diurnal cycle
   - Roel Neggers (neggers@knmi.nl) + Holger Siebert (siebert@tropos.de) baby cloud) + Irina Sandu: Scores of single column regional model

All details on the IMPACT campaign, the payloads of each of the aircrafts, quick looks, logbooks and data can be found at the IMPACT website (http://www.knmi.nl/eucn). For questions on campaign details or login information the contact persons are the IOP project leader Gerd-Jan van Zadelhoff (zadelhof@knmi.nl) and the data base specialist Mark Savenije (Mark.Savenije@knmi.nl). All data will also be stored in the EUCAARI database at NILU.
EVAPORATION OF MIXED INORGANIC/ORGANIC AEROSOL PARTICLES

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Keywords: evaporation, atmospheric aerosols, organic aerosols

INTRODUCTION

Biogenic sources as well as human activities contribute large amounts of volatile organic compounds to the atmosphere. Upon oxidation polyfunctional molecules such as dicarboxylic acids are formed. These molecules generally have lower vapor pressures than the parent molecules and are able to condense on existing particles or maybe even participate in formation of new particles in the atmosphere. Current knowledge about the thermodynamic properties governing this partitioning as well as the influence of the organic molecules on properties of aqueous solution droplets is poor. We have therefore developed a new method for determining the solid and (subcooled) liquid-state vapor pressure as well as other thermodynamic properties of secondary organic aerosol components. We have recently measured evaporation rates of dry particles and aqueous solution droplets containing one dicarboxylic acid (C\textsubscript{3} to C\textsubscript{9}) and water. In this work we broaden the list of compounds under study and point to more complicated systems as dicarboxylic acid together with inorganic salts.

EXPERIMENTAL SETUP

The modified Hygroscopicity Tandem Differential Mobility Analyzer (HTDMA) used in this study is illustrated in Fig. 1. It consists of three interconnected components: (i) a particle generation system where a narrow size range of particles is selected in a differential mobility analyzer; (ii) a laminar flow reactor where particles are allowed to evaporate; and (iii) a second differential mobility analyzer with a particle counter (SMPS system) to monitor the size of the particles by sampling

![Diagram of the modified HTDMA setup at the University of Copenhagen. See text for details.](image-url)
Figure 2: Size spectra of aerosol particles sampled at different ports along the laminar flow reactor (left plot) and time evolution of the particle size obtained converting the port distance in residence time by detailed analysis of the flow regime in the reactor (right plot).

the aerosol flow at different ports along the laminar flow reactor. The basic principles of the experimental system are described in detail in Bilde et al. (2003). For determining the subcooled liquid saturation vapor pressures, the system was recently modified to keep particles as solution droplets in controlled ambient conditions in terms of temperature and relative humidity. (Riipinen et al., 2006; Koponen et al., 2007). Figure 2 shows a typical experimental dataset obtainable with the modified HTDMA: a sequence of size spectra of evaporating particles (left plot) is used to determine the evaporation rate curve (right plot).

**BINARY AND TERNARY INORGANIC-ORGANIC DROPLETS**

Table 1 summarizes our previous and on-going evaporation studies of dry and aqueous solution aerosol particles containing one water soluble organic compound (Bilde and Pandis, 2001; Bilde et al., 2003; Monster et al., 2004; Zardini et al., 2006; Riipinen et al., 2006, 2007; Koponen et al., 2007). The natural step further of this research project is the study of more complex, realistic particles: ternary droplets consisting of one evaporating organic compound, one inorganic non-evaporating salt (i.e. with saturation vapor pressure which are orders of magnitude lower than the detection limit of our setup), and water. The left plot in Fig. 3 shows the evaporation rate of

<table>
<thead>
<tr>
<th>Substances</th>
<th>Formula</th>
<th>M (g/mol)</th>
<th>Evaporation</th>
<th>RH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malonic acid</td>
<td>C₃H₄O₂</td>
<td>104.06</td>
<td>yes</td>
<td>≤ 10⁻⁶, 5-85 °C, 58-80 °C, 70 °C</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>C₄H₄O₄</td>
<td>119.09</td>
<td>yes</td>
<td>40-50-60-65-75-80, ≤ 10⁻⁶, 65 °C</td>
</tr>
<tr>
<td>Keto-succinic</td>
<td>C₄H₄O₄</td>
<td>132.07</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Glutaric acid</td>
<td>C₄H₄O₂</td>
<td>132.12</td>
<td>yes</td>
<td>≤ 10⁻⁶, 65 °C</td>
</tr>
<tr>
<td>α-keto-glutaric (2-oxo-g)</td>
<td>C₅H₄O₂</td>
<td>146.1</td>
<td>yes</td>
<td>40-65</td>
</tr>
<tr>
<td>Acetone-1,3-dicarboxylic acid (3-k-g)</td>
<td>C₆H₈O₃</td>
<td>146.1</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>2-Oxovaleric acid</td>
<td>C₆H₈O₃</td>
<td>116.1</td>
<td>yes</td>
<td>40-50-60-70-80</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>C₆H₈O₄</td>
<td>146.14</td>
<td>yes</td>
<td>≤ 10⁻⁶, 58-80</td>
</tr>
<tr>
<td>4-keto-pimelic</td>
<td>C₇H₁₀O₃</td>
<td>174.2</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Sodium octanoate</td>
<td>C₁₈H₃₂NaO₃</td>
<td>166.2</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Capric acid sodium salt</td>
<td>C₁₁H₁₄NaO₂</td>
<td>194.25</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Sodium dodecanoate</td>
<td>C₁₂H₂₄NaO₂</td>
<td>222.3</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Lauric acid (dodecanoic)</td>
<td>C₁₂H₂₄O₂</td>
<td>200.32</td>
<td>no</td>
<td>40-60-80</td>
</tr>
<tr>
<td>Myristic acid</td>
<td>C₁₃H₂₆O₂</td>
<td>228.38</td>
<td>no meas.</td>
<td>60</td>
</tr>
<tr>
<td>Palmitic acid</td>
<td>C₁₅H₂₈O₂</td>
<td>256.43</td>
<td>yes</td>
<td>60</td>
</tr>
<tr>
<td>Decanoic acid</td>
<td>C₁₄H₂₄O₂</td>
<td>172.27</td>
<td>yes</td>
<td>50-80</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>C₁₇H₃₄O₂</td>
<td>284.49</td>
<td>no meas.</td>
<td>40-50-60-80</td>
</tr>
<tr>
<td>Octanoic Acid</td>
<td>C₈H₁₆O₂</td>
<td>144.21</td>
<td>no meas. (oil)</td>
<td>60</td>
</tr>
</tbody>
</table>

succinic acid/sodium chloride/water particles with different organic to inorganic salt molar ratios of the initial solution. By decreasing the presence of the organic compound, the evaporation rates decrease to such an extent that no evaporation is detectable already at 0.57 organic molar ratio. A very similar behavior is observed when ammonium sulfate is used instead of sodium chloride (not shown here). This interesting result suggests the possibility that the evaporation of organic material away from aerosol particles might be slowed down by the presence of inorganic salts. To better understand these findings, model calculation on the droplet composition (Clegg et al., 2006a,b) have been undertaken. Some preliminary results are shown in Fig. 3: the evaporated mass estimated from the reduction in measured droplets size compared to the total succinic acid mass as predicted by the model is shown in the right panel. The one-to-one correspondence indicates that the evaporated mass can be properly predicted by the model. Further analysis is ongoing to better investigate the role of inorganic salts in evaporation of organic aerosol components.

Figure 3: Evaporation rates (left plot) and model results (right plot) for succinic acid/sodium chloride/water ternary droplets.

ACKNOWLEDGMENTS

This work is supported by the European Integrated project on Aerosol Cloud Climate Air Quality Interactions (EUCAARI), the Nordic Center of Excellence on Biosphere Aerosol Cloud Climate Interactions (BACCI), and the Danish Natural Science Research Council through the Copenhagen Center for Atmospheric Research (CCAR).

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