

## **Minutes of meeting of EUROCHAMP JRA2-WP3 'Techniques for the Evaluation and Development of Aerosol Models', 12-13 February, JRC Ispra.**

The following is a short summary of the meeting of the JRA2-WP3 meeting held in Ispra. The scope of the meeting was to get an overview of ongoing work at the partners, discuss some issues of common interest (ageing, oligomer formation) and to initiate an initiative aiming at intercomparing Secondary Organic Aerosol (SOA) modules by simulation of chamber experiments. The presentations given at the meeting can be found at the web-site <http://www.eurochamp.org/>

### **1. Overview and discussion of ongoing work of the EUROCHAMP partners, related to aerosol modeling.**

*Helmut Bunz and Karl-Heinz Nauman (FZK)* told about studies performed in the AIDA chamber. Experimental as well as modeling work has addressed ice nucleation on soot particles and the influence of H<sub>2</sub>SO<sub>4</sub> and SOA coatings on the capability of dust and soot particles to activate ice nuclei formation. Other studies have dealt with applications of the COSIMA (COMputer SIMulation of Aerosols) model to perform a size-resolved simulation of SOA formation and ageing at different temperatures by ozonolysis of  $\alpha$ -pinene.

*Bart Verheggen (ETH, Zurich)*, presented 'PARGAN', an inverse modeling procedure to determine particle nucleation and growth rates directly from measurements, i.e. without relying on classical nucleation theory and showed results of applying this tool to chamber as well as field observations.

*Elisabetta Vignati (JRC)* gave an overview of the aerosol-related studies carried out in Ispra, with special emphasis on how aerosols are dealt with in the TM5 global chemical transport model and the needs for inputs from laboratory and field studies.

### **2. How can we improve modeling of 'ageing' (changes in hygroscopicity) of Black Carbon and organic aerosol?**

Introduction by *Elisabetta Vignati*

Experimental results on soot aerosol from AIDA: *Karl-Heinz Naumann and Helmut Bunz*

The term BC 'aging' refers to the shifting of black carbon from a hydrophobic to a hydrophilic state. The processes that are responsible of the aging are condensation of soluble material on BC particles, coagulation with other soluble particles and oxidation (e.g. by O<sub>3</sub>) of organic material that coats the particles. Usually the explicit treatment of these processes can be time consuming in large-scale models therefore in many cases models assume that the conversion between hydrophobic to hydrophilic state follows an exponential decay process with a certain half-time, called the 'aging time'.

Independently on how the aging is modeled some assumptions are required:

1) the assumption of BC particles as spheres instead of fractal structures - microscopic view of the soot particles show that fresh soot particles have a fractal form while aged particles assume a more spherical shape: when a soluble layer coats the particles the fractal structure crashes into a more spherical one

2) the definition of the transition between soluble and insoluble BC particle: for instance, is it correct to assume that when a monolayer of soluble material covers the particles they are soluble? It would be important to know also:

3) if at atmospheric conditions oxidation and aerosol dynamics compete with each other and which of the two would be the most efficient in aging BC.

The smog-chamber experiments can help in finding the answers, even though they have to be performed in atmospheric conditions to give the most useful information.

The work done in Karlsruhe using the model COSIMA (COMputer SIMulation of Aerosols) show that the fractal structure enhances coagulation rates, reduces particle mobility, reduces wall losses due to sedimentation and diffusion compared to compact spherical particles.

The experiments done in the AIDA aerosol chamber show that the collapse of particle aggregates into spheres coated by non absorbing material causes also a change in the particle optical properties: increase of single scattering albedo and absorption. The increase of the coating thickness causes an increase of extinction and scattering. In this case soot particles can be represented by sphere.

### **3. Intercomparison of existing SOA-modules**

*Jens Hjorth* explained the intentions of the JRC regarding the proposed intercomparison exercise: The idea is to test existing modules for simulation of secondary organic aerosol (SOA) formation in atmospheric models against experimental data from a set of selected chamber experiments, with the scope of obtaining a more systematical picture of the uncertainties on SOA-modeling and to get a basis for analysing the differences between the different modelling approaches and possibly improve the models. The EUROCHAMP database on observations from chamber experiments would be used as the main source of experimental data for this exercise.

*Matthias Karl* gave an overview of existing SOA models:

Most SOA models use an equilibrium approach for the treatment of the uptake and release of gases in particles; an exception is the one developed by Kamens and coworkers, that treats adsorption and desorption on particles as kinetic processes. Chemistry is treated in various degree of detail both for what concerns the representation of precursor VOC compounds (different classes of terpenes and aromatics, plus isoprene), their reactions and their condensable products. The most detailed treatments of gas phase chemistry related to SOA formation are those of the Master Chemical Mechanism (MCM) and of the Caltech Atmospheric Chemistry Mechanism (CACM). The most widely used representation of the condensable products uses two surrogate semivolatile compounds with yields and partitioning coefficients determined empirically by performing a best fit to data from chamber experiments. Studies have shown (Pun *et al.*, 2003), that a more detailed representation of chemistry can make a large difference, however such approaches involve many assumptions regarding yields and partitioning coefficients ( $K_p$ 's). Some models apply a multiphase (gas, organic, and aqueous phase) treatment of SOA. Recent studies have shown the potential importance of isoprene and benzene as aerosol precursors and has provided other potentially, important new information about SOA-chemistry, particularly regarding the potential importance of oligomerisation reactions (apparently acid-catalyzed), multiphase partitioning and heterogeneous chemistry as well as on the influence of  $\text{NO}_x$ -levels and UV-light on SOA yields. Recent studies suggest that volatile species (e.g. aldehydes, unsaturated hydrocarbons) may participate in oligomerization/polymerization reactions after uptake on particles. Much of this new information still needs to be adequately represented in models.

*David Simpson* told about modeling of carbonaceous aerosol using the EMEP MSC-W model: This model is based on the approach of Kamens *et al.* (1999). The chemical reaction scheme is an expanded version of the simplified, explicit scheme proposed by Kamens; particularly the addition of reactions forming stable dimers was found to cause a considerable increase in the formation of

SOA. The model shows good agreement with smog chamber experiments on alpha-pinene and it reproduces measured Total Carbon in aerosols rather well at some field sites. However, the CARBOSOL project showed that the EMEP model tends underestimate both biogenic and anthropogenic SOA considerably under ambient conditions. Also other comparisons of modelled to experimental SOA data in recent studies show that the models dramatically underestimate SOA levels (underestimation by a factor of 10 or more are not unusual). Some observations suggest that most ambient SOA is highly oxidized organic species and humic like substances, it is important to understand how these substances are formed from the less-oxidized primary products observed in smog chamber experiments.

For the EUROCHAMP exercise, David Simpson proposed to evaluate the  $\alpha$ -pinene scheme against newer smog chamber data and against the Master Chemical Mechanism (MCM).

*Kostas Tsigaridis* talked about the use of the two-product simulation of SOA formation and the results he and Maria Kanakidou have obtained by application of this in models (TM3, TM4): The enthalpy of evaporation of the SOA-components is an important parameter, a change in this (and thus in the temperature-dependence of the partitioning coefficient) leads to important changes in the vertical distribution of SOA. The reasons for the discrepancies between existing SOA models and observations may lie both in an insufficient understanding of formation pathways (gas-, multiphase and aerosol phase chemistry) and in an incomplete knowledge of the precursor compounds. Among the important open questions to be answered how fast equilibrium is achieved and the role of reactions that inhibit evaporation (oligomerization and other chemical transformations, e.g. by cloud processing). The influence of  $\text{NO}_x$ -levels are included in the present model, but other parameters (UV-light, water,...), need to be considered. Other important issues are how to treat product yields from different oxidants ( $\text{O}_3$ , OH,  $\text{NO}_3$ ) and how to deal with second/third.... generations products.

*Mike Jenkin* could not be present at the workshop but sent a briefing note on simulations of SOA formation based on use of the MCM: MCM contains chemical reaction mechanisms for the ozonolysis of  $\alpha$ - and  $\beta$ -pinene as well as the photooxidation of aromatic hydrocarbons. SOA yields were calculated based on these mechanisms combined with equilibrium partitioning coefficients ( $K_p$ ) calculated by use of the method of Pankow (1994), using estimated subcooled liquid vapour pressures and other estimated parameters. However, comparison to smog chamber experiments showed that the estimated partitioning coefficients had to be multiplied by factors of 10 or more in order to reproduce experimental results; a comparison to field data showed an even larger underestimation of the partitioning of products into the aerosol phase.

Concerning the EUROCHAMP exercise, Mike Jenkin did not find it useful to do further testing against smog chamber data of the approach adopted with the MCM; he would rather encourage experiments on simple VOC systems with a limited number of products participating, in order to gain new information on the mechanisms involved in SOA-formation, particularly for what concerns oligomerisation mechanisms (e.g. oligomers of glyoxal) .

*Elena Gómez Alvarez* informed briefly about the EURUCHAMP database on environmental chamber studies, that provides easy access to data records and associated calibration files. The database is based at the CEAM institute in Valencia (Spain)

#### *Discussion:*

It was agreed that the intercomparison exercise should start with just focusing on data regarding one terpene ( $\alpha$ -pinene) and one aromatic compound (toluene) but under a wide range of physical and chemical conditions (temperature, UV-intensity, humidity,  $\text{NO}_x$ -level, ...). Experiments with close-to-ambient concentrations of reactants would be preferred. In the case of  $\alpha$ -pinene, reactions with

ozone, OH and NO<sub>3</sub> would be of interest while for toluene only OH is relevant. Relevant data sets will be searched on the EUROCHAMP database but also by directly taking contact to relevant institutes. In addition to these experimental data, also as much information as possible about relevant chamber artefacts (wall source of OH, dilution rate,...) and wall loss rates should be collected. In the case of EUPHORE, chamber-specific reactions are described on the MCM website (<http://mcm.leeds.ac.uk/MCM/MCMChamber.htm>).

It is intended to involve as many different models as possible in this exercise. In addition to those represented at the meeting, Colin O'Dowd has expressed interest in participating with the SOA scheme in the REMOTE regional climate model. Other European as well as US modelers will be contacted.

JRC and CEAM will start collecting relevant simulation chamber data sets and contacting modeling groups to invite them to participate. The collection of data sets should be finished after 6 months, by then the participating groups will be invited to simulate selected chamber experiments. Finally, differences between models and between models and experiments under different conditions and at different timescales will be carefully analysed.

In the discussion, the point was raised, that it might be worthwhile to look into the reasons why the K<sub>p</sub>'s estimated by Mike Jenkin using the method of Pankow appear to be much lower than those estimated using the approach of Kamens (also used in the EMEP model).

#### ***4. How can we approach modeling of oligomer formation?***

*Axel Metzger (PSI)* informed about experimental results from the PSI smog chamber that may have consequences for SOA-modeling; particularly regarding observations of oligomer formation. He also discussed ongoing work on the observations of dimers and on the influence of SO<sub>2</sub> on SOA formation:

Oligomerization has been observed by Laser Desorption Ionization in SOA from monoterpenes, isoprene as well as aromatic precursors. The chemical processes involved in the oligomer-formation are not clarified and recent high-resolution mass spectrometry measurements have shown that the variety of different oligomers formed is larger than believed previously.

Several observations have been made, that may be useful for understanding how to approach modelling of oligomerization: The type of growth of the oligomers is characterized as 'chain growth', where the oligomerization is initiated by a few active sites (e.g. radicals) and large molecular size oligomers are formed early in the experiment (as opposed to 'step growth', where a large number of monomers initiate oligomerization). An increase in oxidized functional groups is observed during the experiments. On the other hand, mass spectrometrical analysis suggest that the O:C ratio tends to decrease with increasing oligomer size (as would be the case if oligomers are formed by condensation reactions with elimination of e.g. water). Hygroscopic growth of the SOA particles at sub- and supersaturated conditions (observed by HTDMA and CCN Counter instruments, respectively) increases during the experiment (lights are on in the chamber). An influence of precursor concentrations is observed, where high concentrations give lower hygroscopicity (possibly because of condensation of more volatile/less oxidized/less water soluble products).

A first attempt to model oligomer formation has been made by Pun et al. (2007), based on the comprehensive literature on studies of such reactions that have appeared in the latest years. In this work, oligomerization is treated as an acid-catalyzed, reversible process that may be represented in models by an 'effective partitioning coefficient'.

There appeared to be general agreement on the suggestion by Mike Jenkin to encourage more experimental (chamber) studies on SOA-formation in simple, well-defined systems, to get a better basis for characterizing all relevant processes..

## **5. *General discussion***

It was agreed to make all presentations available on the EUROCHAMP web-site.

A second meeting of this Work Package will be held when there is a basis for discussing results of the SOA modelling intercomparison exercise.

Jens Hjorth, Matthias Karl and Elisabetta Vignati, Ispra 14./3./2007