MINUTES OF EUROCHAMP MEETING ON TESTING OF SOA MODELS AGAINST CHAMBER EXPERIMENTAL DATA

Hotel Concorde, Via Verbano 1, I- 28041 ARONA (NO)

AGENDA

***Wednesday April 29*.**

13:30 – 14:00 Welcome and introduction to the SOA model/chamber experiment intercomparison exercise/Jens Hjorth

14:00 – 14:30 Introduction to the EUROCHAMP database on environmental chamber studies/ Elena Gomez Alvarez

14:30 -18:00 Presentations from participating modelers of their SOA model and of results of the first simulations of chamber experiments within this exercise.

Coffee Break at 16.00-16.30

Dinner at 20:00 in the restaurant of Hotel Concorde.

Thursday April 30

9:00-10:30 What can be learned from the first simulations of chamber experiments?

10:30-11:00 Coffee break

11:00-12:30 Continuation of the model/chamber data intercomparison exercise: Which chemical systems should be addressed?

12:30-14:00 Lunch

14:00-16:00 Planning of future work. Which experimental information should be made available to the modelers?

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PARTICIPATING MODELS IN THE PRELIMINARY ROUND OF CHAMBER MODELING STUDIES

B. Aumont/ M. Camredon/R. Valorso
GECKO-A: **G**enerator for **E**xplicit **C**hemistry and **K**inetics of **O**rganics in the **A**tmosphere

Henri Vuollekoski/ Michael Boy
MALTE – Model to predict new Aerosol formation in the Lower Troposphere

K. Ceulemans/S. Compernolle/ L. Vereecken, J. Peeters
BOREAM model

Matthias Karl
TM5-SOA Box Model

Tove Svendby
MAPSv1.2

Kostas Tsigaridis/Mihaela Mircea/ Maria Kanakidou
2-PRODUCT SOA APPROACH

Karl-Heinz Naumann
COSIMA

Robert Bergström/David Simpson
EMEP model

Gordon McFiggans
Dave Topping
Aerosol modeling based on the MCM

PRESENTATIONS OF THE INDIVIDUAL GROUPS

JENS HJORTH: INTRODUCTION TO THE INTERCOMPARISON OF SOA-MODULES

JH gave an overview of the main aspects of the exercise:

Scope of the exercise:
- To see how well existing models of SOA formation can simulate chamber experiments
- Analyse reasons for the differences between models

Why use chamber data?
- Controlled conditions
- Chemistry can be separated from transport

Disadvantages: Wall effects need to be considered, concentrations are typically higher than ambient

Experimental data used in this exercise:
- ozonolysis of α-pinene at EUPHORE with CO as OH-scavenger
- ozonolysis of α-pinene at AIDA, no OH scavenger
- photooxidation of α-pinene in a NOx/air mixture at the PSI

Why doing this intercomparison in the framework of EUROCHAMP?
The EUROCHAMP database is an ideal source of experimental data, also containing information relevant for quality assurance.
EUROCHAMP makes it possible to compare similar experiments performed in different chambers and thus to get an idea about chamber-dependent biases.

ELENA GÓMEZ ALVAREZ: THE EUROCHAMP CHAMBER EXPERIMENT DATABASE: GOALS AND USES. PRESENT AND FUTURE POTENTIAL BENEFITS

EGA gave an overview of the EUROCHAMP database on environmental chamber studies explaining its main present uses and potential future advantages and benefits of its use.
In the round of questions, she is asked how the quality of the datasets included in the database are guaranteed, to which EGA answers that exercises like the aerosol Intercomparison is a good way to revise and cross-check data.
Some comments point in the direction that the database is not sufficiently being advertised in other venues/contexts except for the members of the EUROCHAMP Consortium. It was proposed that Elena and the project co-ordinator, Peter Wiesen should meet the co-ordinators of the EUSAAR and EUFAR projects, under which frame databases including field data studies and aircraft studies have been developed, in order to discuss a coordinated effort to make these data bases known to potential users. There could be a number of practical difficulties, for example there is no homogeneity in the format of the data of the individual databases (EUSAAR uses the NASA Ames 1001 data format, EUROCHAMP has developed a special data format for its database).

BERNARD AUMONT : GECKO-A, AN EXPLICIT MODELLING TOOL TO EXPLORE THE SOA/VOC/NOX SYSTEM

GECKO-A (described in Aumont et al., ACP, 2005) is an expert system that:
- assimilates physical and chemical data from laboratory experiments
- estimates the missing information based on structure/activity relationships (SAR)

The protocol currently used is conceptually similar to the MCM3 mechanism. Most SARs implemented were borrowed from SAPRC99, MCM and NCAR MM.

1. Gas phase oxidation schemes

Explicit description of the production and removal of semivolatile organic compounds (SVOC) in the gas phase based on GECKO-A

2. Gas/particle partitioning of SVOC

Phase equilibrium described on the basis of Raoult's law:
- Assume a thermodynamic equilibrium between gas and particulate phases
- P_{vap} are estimated for each intermediate using Myrdal & Yalkowsky (1997) structure/properties relationship [Camredon et al., Atmos. Env., 2006]

Conclusions from the preliminary simulation of chamber runs

The SOA concentration was overestimated for the PSI runs, however or the rest of the species (α-pinene, ozone, NO and NO_2), the agreement between modelled and experimental data was quite good. The simulated SOA values were closer to the true values in the EUPHORE runs and strongly underestimated in the AIDA experiment.

HENRI VUOLLEKOSKI, MICHAEL BOY: MALTE – MODEL TO PREDICT NEW AEROSOL FORMATION IN THE LOWER TROPOSPHERE

- 1 or 0-dimensional model
- Chemistry (KPP-MCM)
- Aerosol dynamics (UHMA)
- Multicomponent condensation
- Several nucleation theories

Vapours contributing to particle growth are sulphuric acid, ammonia, water and an unspecified number of water-soluble and water-insoluble organic compounds

[C]Vapour1 = Y1 * [Monoterpenes] * [O3], [OH], [NO3]
[C]Vapour2 = Y2 * [Monoterpenes] * [O3], [OH], [NO3]

Y1 = 0.05 (condensing on nano-sized inorganic clusters)
Y2 = 0.1 (involved in the general condensation mechanism)

Only first order reaction products taken into account.

Change rate in particle volume = collision rate between particles and gas molecules x gas molecule volume x (gas concentration – gas saturation concentration)

Conclusions from the preliminary simulation of chamber runs

Particle numbers are somewhat overestimated, but a part of the size-distribution is well reproduced.

K. CEULEMANS, S. COMPERNOLLE, J.-F. MÜLLER: SIMULATION OF SMOG CHAMBER EXPERIMENTS FOR α-PINENE WITH BOREAM MODEL

Quasi-explicit treatment of chemistry (~5000 reactions, 1300 species). Partitioning follows a kinetic representation with coefficients calculated by a group contribution method.

Conclusions from the preliminary modelisation of chamber runs

- AIDA dark ozonolysis:
  - Ozone decay modelled well, α-pinene decay slightly overestimated
  - SOA: underestimated by about factor 2-3
  - This model behaviour was also seen for other dark ozonolysis experiments with T higher than 303 K and low initial VOC
- Euphore dark ozonolysis:
  - Some uncertainty about experimental data such as initial concentrations of α-pinene. They requested revision of these data. With assumption of higher initial VOC concentration –including the estimation of pinonaldehyde which is suspected to lump other species, quite acceptable results are found.
  - For aerosol mass, good agreement is observed but depends on assumptions for wall losses
- PSI photolysis
  - With $J(NO_2)$ = 0.0016/s (Metzger et al. 2008): α-pinene oxidation far too fast, ozone overestimated
  - Lower $J(NO_2)$: more acceptable, but there are still discrepancies for the key species
  - Some uncertainty about light spectrum and about wall reactions

MATTHIAS KARL: TESTING OF SOA MODELS AGAINST CHAMBER EXPERIMENTAL DATA

TM5-SOA Box Model

The model uses an approach, where each oxidation reaction produces two semivolatile products that are partitioned between the gas- and the condensed-phase.

$$\mathrm{VOC}_i + \mathrm{OX}_j \rightarrow \alpha_{i,j,1}\mathrm{P}_{i,j,1} + \alpha_{i,j,2}\mathrm{P}_{i,j,2}$$

$$G_i = \frac{A_i}{K_{p,i} M_o}$$

The gas/aerosol partitioning depends on temperature and the concentration of pre-existing organic mass.
The model accounts for the temperature dependence of chemical reactions and partitioning coefficient and applies NOx-dependent yields and partitioning coefficients for condensable products. The chemical mechanism is Carbon Bond IV.

Conclusions from the preliminary simulations of chamber runs

- Difficulties to model α-pinene decay in EUPHORE and AIDA experiments.
- PSI: uncertainties in modeling photolysis rates? What about $J(O^1D)$?
- Need to update $k(NO+O_3)$, $k(NO_2+OH)$, $k(NO_2+O_3)$ etc. in model.
- SOA from photo-oxidation (PSI) and ozonolysis experiments (EUPHORE) clearly better matched when VOC/NOx dependence is included.

TOVE M. SVENDBY, NILU: EUROCHAMP TESTING OF SOA MODELS AGAINST CHAMBER EXPERIMENTAL DATA

MAPSv1.2

- Model for Aerosol Process Studies (MAPS).
- Developed at NCAR, USA.
- Box model with gas/aerosol chemistry.
- Gas phase photochemistry (SAPRC-97/99 mechanism).
- Includes condensation, evaporation, deposition.
- Partitioning coefficients are T-dependent

In MAPS it is assumed that two "representative" oxidation products are formed, i.e. the same approach as in the TM5 model
Yield and partition functions are based on Odum et al., 1996 and makes use of Ki(T), partition coefficient for product *i*. Temperature dependence is from Sheehan and Bowman, 2001.

Conclusions from the preliminary modelisation of chamber runs

- The modelled a-pinene decay is too high in the dark experiments (Reaction rates from Khamaganov and Hites, 2001, and Atkinson, 1997, give similar results).
- Modelled SOA formation in dark experiments is in good agreement with measurements.
- Preliminary results from photo-oxidation experiments indicate that modelled SOA is highly overestimated

MIHAELA MIRCEA: PSI CHAMBER EXPERIMENTS PRELIMINARY RESULTS WITH A BOX MODEL BASED ON 2-PRODUCT SOA APPROACH

The model uses a two condensable products approach, similar to TM5-SOA and MAPS.
A sensitivity study showed that the choice of equilibrium partitioning coefficients, among those published in the literature,could change calculated SOA yields significantly (differences of more than 30%). Also the dependence of SOA yields on

temperature variations was tested. The influence of the choice of starting point for the simulations was also tested.

Conclusions from the preliminary modelisation of chamber runs (PSI experiments)

- Model reproduces better the experiment 1/8/2007 than 4/6/2007
- Maximum SOA mass concentrations predicted by model are more close to the maximum concentrations measured when the simulations start after 7200s
- An important reason for the differences in SOA mass concentrations between model and experiment may be that the temperature used in the model is incorrect.

KARL-HEINZ NAUMANN (K-H.N): MODELLING OF SOA EXPERIMENTS WITH COSIMA

COSIMA (COmputer SIMulation of Aerosols)

COSIMA SOA Parameterization: Simulation based on a two condensable products model.
Structure, dynamics, optics, and heterogeneous chemistry of agglomerate and SOA containing particles treated using fractal scaling laws. It makes a kinetic treatment of the uptake and release of gases from particles.
Product parameters fixed beforehand (not fitted to measured data):

- Molar mass: M1 = 186 g/mol, M2 = 168 g/mol (both α-pinene and limonene cases).
- Gas phase diffusion coefficients from Chapman-Enskog theory and Lennard-Jones parameters (0.040 – 0.056 cm2/s).
- Bulk density from AMS / SMPS measurements: 1.25 g/cm3 (α-pinene), 1.3 g/cm3 (limonene).
- Surface tension: s1 = 80 dyn/cm, s2 = 30 dyn/cm (both α-pinene and limonene cases)

Conclusions from the preliminary simulations of chamber runs (AIDA and EUPHORE experiments only)

- The SOA yields for ozonolysis of α-pinene and limonene measured in the AIDA chamber can be accurately reproduced by a 2-component approach.
- The observed SOA yields are significantly affected by wall losses of the more volatile condensable product(s) in the gas phase. This is especially true at elevated temperatures. Detailed modelling essential to reliably account for direct wall losses.
- The time evolution of the SOA number concentration is very sensitive to the vapour pressure of the product with lowest volatility and – to a lesser extent – to its surface tension. Kelvin effect has to be accounted for.
- The SOA yields determined during the two EUPHORE experiments considered in this intercomparison exercise can be reproduced by a 2-component approach.

ROBERT BERGSTRÖM, DAVID SIMPSON: EVALUATION OF GAS/PARTICLE SOA MECHANISMS FOR A-PINENE FOR THE EMEP MODEL

Standard EMEP SOA box-model photochemistry scheme

Coupled scheme VOC - NOx - CO - SOx – NHx.
Standard version includes

- Ca 60 different chemical components
- Ca 110 thermal, gas-phase, reactions
- Ca 25 photolysis reactions
- Aqueous phase oxidation of SO_2
- (simplified) heterogeneous reactions (including NHx chemistry)
- Basic idea is to use a limited number of "representative" VOCs to model all emitted VOC. The selection of model VOCs is based on Photochemical Ozone Creation Potentials (POCPs)

KPP Kinetic Pre Processor used to construct the ODE solver for the chemistry.
EMEP GENCHEM (alternative solver pre-processor by D. Simpson, used for the EMEP 3D-model)

Simulations by two different versions of the model were compared, both based on the work of Kamens and co-workers (Kamens and Joui, 1001; Le et al., 2007).

Conclusions from the preliminary modelisation of chamber runs

- PSI Simulations
  - Both models show important discrepancies. The bigger discrepancies are found for the experiment performed on 06/04/2007
  - In the simulations of SOA mass, error bars are included what brings the experimental observations closer to some of the models predictions
  - The predictions improve slightly when a lower $J(NO_2)=0.0009\ s^{-1}$ is applied

- EUPHORE (2002/01/16; 2002/01/11)
  - The predictions show higher discrepancies but there are doubts about starting conditions (The injection time is taken as starting point and a concentration of 55.76 ppb, on 2002/01/11). No wall losses or dilution have been taken taken into consideration in the predictions

GORDON MCFIGGANS: CHAMBER MODELLING AT MANCHESTER WITHIN EUROCHAMP2

SOA CODE FOR MCM V3.1

GMcF presented the planned contribution of Univ. of Manchester to EUROCHAMP-2. He discussed results from the ACES project, a Consortium project within the APPRAISE programme, in particular from chamber studies of biogenic VOC emissions and SOA formation. He also explained aspects related with the Development and application of SOA code for MCM v3.1.

DISCUSSION

After all the presentations JH starts by summarising some of the conclusions from the preliminary comparison between model and chamber data:

PSI photo-oxidation experiments:
SOA formation overestimated by nearly all models. Better agreement was obtained by reducing J(NO2) in the models. Spectral distribution different from sunlight?
Reasonable agreement was obtained by TM5 model when NOx-dependence of SOA yield was taken into account.
EUPHORE ozonolysis experiments (CO as OH scavenger)
Quite good agreement for the 2-product models COSIMA and MAPS; TM5 performs slightly better with NOx-dependence included
No systematical under- or overestimation of SOA by models
AIDA
Good agreement with COSIMA and MAPS.
Explicit models strongly underestimate aerosol yields

Some general observations could be made:

- models assuming gas-particle phase equilibrium seem to perform reasonably well, at least for some of the experimental conditions
- evidence of importance of [NOx]/[VOC]
- wall-losses of semivolatile compounds seem to be important (COSIMA)
- there are cases of strong disagreement between model simulation and experiment that need to be analysed further

It is-at the present stage- not clear to which extent differences between models and experimental results may be explained simply by the influence of wall losses and errors in the representation of photolysis rates. Thus, it was generally found important to get more detailed information about experimental conditions and characteristics of the chamber needed, particularly:
-Wall loss rates for different types of compounds (vapour pressures, polarity)
-Photolysis rates/spectral distribution of lamps

It was generally agreed that it would be useful to continue the present intercomparison exercise, within the framewrok of EUROCHAMP-2, if possible.
In relation to future activities, the following points were addressed:

1. It was discussed if the MUCHACHA campaign data could be used for a model intercomparison. Finally, this approach was discarded for now, because of the relatively long time it will take to get the data available. It was agreed to start working with data that are already available.
2. A proposal for carrying out a number of experiments for characterisation of chamber artifacts was discussed. One of the issues would be to measure wall losses of selected compounds in different chambers (volatile compounds like acetone as well as semivolatiles like pinonic acid). Possibly also a series of replicate experiments on SOA formation from a well-defined chemical system (e.g. ozonolysis of α-pinene) in different chambers could be carried out. Robert

Bergström from the University of Gothenburg volunteered to prepare a proposal of this type for a Transnational Activity within EUROCHAMP-2.

3. EGA is to send a message to the members of the Intercomparison team whenever suitable experiments of ozonolysis or photo-oxidation of α-pinene or isoprene are detected
4. Experiments for which we have extensive information about speciation in the gas and particle phases will be highlighted.
5. Some new α-pinene experiments have been or are soon going to be introduced in the database, coming from different institutions:

- IFT in Leipzig has introduced two experiments on α-pinene

-Univ. of Manchester (GMcF) informed that soon (within about two months), they will have a relatively large set of experiments on α-pinene in the database.

-AIDA also has a set of about 20 experiments on α-pinene to introduce in the database

GMcF asked EGA if it would be possible to obtain help in man-power introducing the data in the database. To what EGA replies that guidance can be provided at all times, but that it is not among the tasks of the EUPHORE database administrators to introduce the data of the different institutions into the database. Each institution is responsible for its own data. EGA also emphasizes that the data to be used should be included in the database and not be distributed through other channels. The EUROCHAMP database should be the frame under which the exercise is carried out and the only source of data.

6. A few data are missing to complete and finalise the first round of modeling studies. The data missing are in particular:

-J(NO_2) from PSI.

-Check initial experimental concentration values of α-pinene in the experiment performed 11/01/02, and clarify which data should be used by the modellers.

-Documentation of chamber characterisation of wall losses (EGA will send it to JH)

-Check the high values of pinonaldehyde provided for 16/01/02 and 17/01/02

7. Bernard Aumont: comments that there should be error bars in the model studies

CONCLUSIONS

- The present model intercomparison can be finalized after the requested information has been provided to modelers.
- It was found that a more efficient and interactive communication between modelers and chamber ‘owners’ would be useful to ensure that relevant experimental datasets are known by modelers.
- The analysis of the results obtained within this exercise showed that a knowledge of wall deposition rates, particularly for semivolatile organics, appear to be important for improving the simulations of SOA-formation in chambers. Also an accurate characterisation of the chamber light source appear to be important.
- It was recommended to EUROCHAMP-2 to continue SOA model/chamber data intercomparison activities, taking advantage of the possibilities offered by the EUROCHAMP data base.

Elena Gomez Alvarez and Jens Hjorth