Amine photo-oxidation experiments: Size-resolved aerosol modeling

Matthias Karl[1,*] and Claus Jørgen Nielsen[2]
[1]Norwegian Institute for Air Research (NILU), Kjeller, Norway
[2] CTCC, Department of Chemistry, University of Oslo, Norway
* mka@nilu.no

1. Motivation

Amine technology to absorb CO_2 from gas-fired power plants is planned in Norway. From a single plant, about 40 tonnes of amines are expected to be released to air per year. Due to their low vapour pressure and high solubility amines will condense to particles and partition to aqueous phase of particles (Fig. 1). Both formation of new particles and secondary organic aerosols was observed in earlier experiments [1,2,3,4].

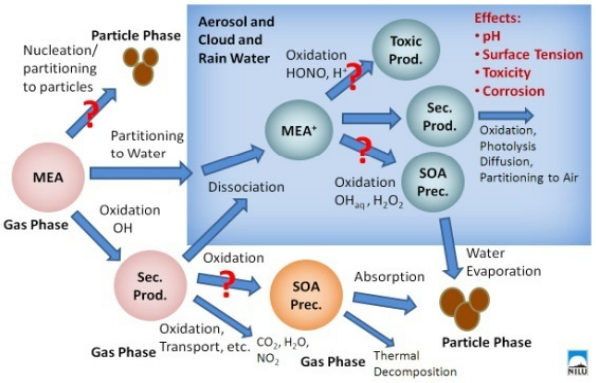

Figure 1: Possible gas/particle/aqueous phase reactions for Monoethanolamine (MEA).

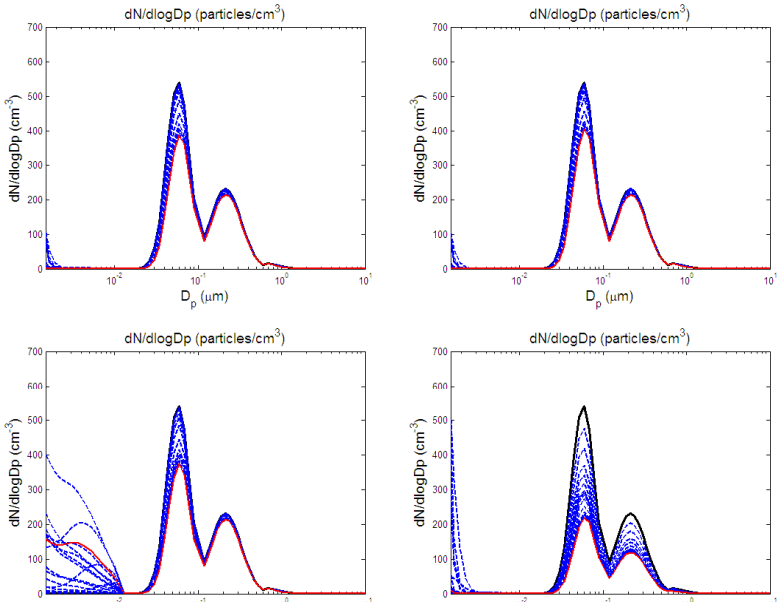

Figure 3: Test of aerosol processes with MAFOR: a) nucleation-condensation-coagulation, b) no coagulation, c) no condensation, d) all processes including wet deposition. Black line: initial distribution, red line: final distribution, dashed blue lines: hourly distributions during the simulation.

2. Aerosol model processes

A new sectional aerosol chemistry and dynamics box model was developed for this study: MAFOR (marine aerosol formation). The general dynamic equation is solved for the size distribution of a mixed multi-component aerosol. Included processes are the same as in the monodisperse model MONO32 [5,6]: 1) gas phase chemistry, 2) binary nucleation of sulfuric acid/water, 3) condensation of sulfuric acid and MSA onto particles, 4) coagulation, 5) dry and wet deposition of particles.

3. Testing

A 80-hour MBL simulation for an arctic aerosol (scenario see Karl et al., 2007 [7]) was performed with both aerosol models. Calculated final number size distribution (Aitken, accumulation, coarse mode) of MAFOR compare well with MONO32 (see Fig. 2). Increasing number of size bins in MAFOR from 60 to 500 has negligible effect on the distribution. Numerical diffusion is reduced in MAFOR by allowing the diameter to move inside the sections. Aerosol dynamics in MAFOR were tested by switching off processes (Fig. 3). Condensation of H_2SO_4 prevails the number size distribution in the arctic simulation.

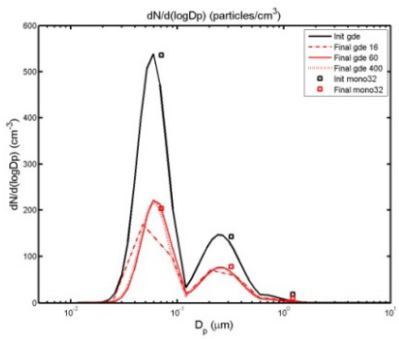

Figure 2: Initial and final size distribution from MONO32 and MAFOR (using 16, 60, and 400 size bins).

4. CH_3NH_2+HONO Experiment

Experiments with alkyl amines were carried out in the Euphore photo reactor. The amine and HONO was injected into the dark chamber. Possible particle growth mechanisms after opening the canopy:

a) Intense nucleation (amine-HNO_3 clusters)
b) Condensation of low volatile amine oxidation product to particles
c) Amine+HNO_3 gas-to-particle equilibrium
d) SOA gas/particle partitioning

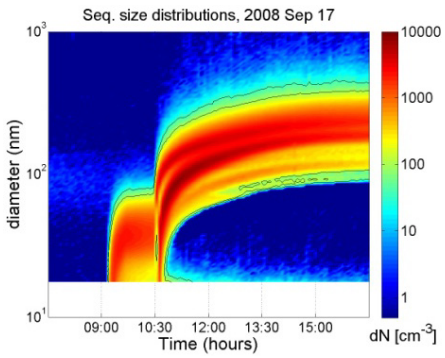

Figure 4: Particle formation from CH_3NH_2+HONO photo-oxidation experiment. Chamber opening at 10:27 local time.

Start	End	Step
07:46	08:13	Addition of CD_3NH_2
09:09	09:41	HONO injection
10:27	10:27	Chamber opened
15:03	15:03	Chamber closed

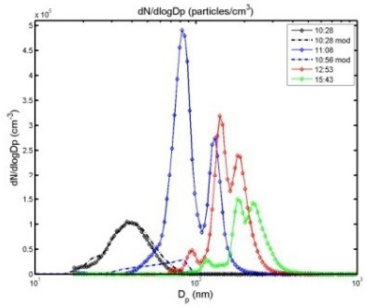

Figure 5: Modeling the temporal evolution of particle number concentrations from CH_3NH_2 photo-oxidation after chamber opening. Included processes: 1) amine+HNO3 gas-to-particle equilibrium, 2) condensation of low volatile amine oxidation product. Simulated amine+HNO3 equilibrium not sufficient to reproduce observed accumulation mode number concentrations. Declining number concentrations after 12:30 due to wall loss and evaporation of alkylammonium nitrate particles.

5. Future Developments

- Constrain model run with measured gas phase concentrations of reactants.
- Dilution of gas phase species, wall losses of amine and particles.
- Two-product model to describe SOA partitioning from amine oxidation
- Include gas/particle partitioning of amine-SOA.
- Include chemistry of amines in the a) gas phase, and b) aqueous phase.

References

[1] Pitts, J. N., Grosjean, D., Vancauwenberghe, K., Schmid, J. P. and Fitz, D. R. 1978: Photo-oxidation of aliphatic amines under simulated atmospheric conditions – formation of nitrosamines, nitramines, amides, and photo-chemical oxidant; *Environ. Sci. Technol.*, 12(8), 946-953.
[2] Angelino, S., Suess, D. T. and Prather, K. A. 2001: Formation of aerosol from reactions of secondary and tertiary alkylamines: Characterization by aerosol time-of-flight mass spectrometry; *Environ. Sci. Technol.*, 25(15), pp. 3130.3138.
[3] Mäkelä, J. M., Yli-Koivisto, S., Hiltunen, V., Seidl, W., Swietlicki, E., Teinilä, K., Sillanpää, M., Koponen, I. K., Paatero, J., Rosman, K. and Hämeri, K. 2001: Chemical composition of aerosol during particle formation events in boreal forest; *Tellus*, 53B, pp. 380-393.
[4] Murphy, S. M., Sorooshian, A., Kroll, J. H., Ng, N. L., Chhabra, P., Tong, C., Surratt, J. D., Knipping, E., Flagan, R. C. and Seinfeld, J. H. 2007: Secondary aerosol formation from atmospheric reactions of aliphatic amines; *Atmos. Chem. Phys.*, 7, pp. 2313-2337.
[5] Pirjola, L. and Kulmala, M. 2000: Aerosol dynamical model MULTIMONO; *Boreal Environ. Res.*, 5, pp. 361-374.
[6] Pirjola, L., Tsyro, S., Tarrason, L. and Kulmala, M. 2003: A monodisperse aerosol dynamics module, a promising candidate for use in long-range transport models: Box model tests; *J. Geophys. Res.*, 108(D9), 4258, doi:10.1029/2002JD002867.
[7] Karl, M., A. Gross, C. Leck, and Pirjola, L. (2007), Intercomparison of dimethylsulfide oxidation mechanisms for the marine boundary layer: Gaseous and particulate sulfur constituents, *J. Geophys Res.*, 112, D15304, doi:10.1029/2006JD007914.