Modelling of Secondary Biogenic Aerosols

T. M. Svendby[1], and M. Lazaridis[2]

[1] Norwegian Institute for Air Research (NILU), P.O. Box 100, NO-2027, Kjeller, Norway - *www.nilu.no*
[2] Technical University of Crete, Department of Environmental Engineering, Polytechneioupolis, 73100, Chania, Greece

Introduction

An important problem in atmospheric chemistry is to improve our understanding of secondary organic aerosol (SOA) formation. In the current work we present recent advances in the development of an efficient and realistic model for SOA formation which is tested against several gas chamber experiments. The work is based on the MAPS model, extracted from the 3D-air quality model UAM-AERO (Kumar et al., 1995), and the SAPRC-97 mechanism.

In this work we focus on two groups of VOC's (terpenes and aromatics) which produce aerosols through oxidation processes. Comparisons between model simulations and experimental data from smog chambers reveal that the existing yield functions in MAPS need modifications.

The model

The SAPRC-97 mechanism in MAPS (Model for Aerosol Process Studies) includes eight groups of VOC's that can form secondary organic aerosols through reactions with OH, O_3, NO_3, or O:

SOA1: CRES + OH	(cresols)
SOA2: ALK1 + OH	(less reactive alkanes)
SOA3: ALK2 + OH	(more reactive alkanes)
SOA4: ARO1 + OH	(less reactive aromatics)
SOA5: ARO2 + OH	(more reactive aromatics)
SOA6: OLE1 + OH, O_3, NO_3, O	(less reactive alkenes)
SOA7: OLE2 + OH, O_3, NO_3, O	(more reactive alkenes)
SOA8: OLE3 + OH, O_3, NO_3, O	(monoterpenes)

Yield

Secondary organic aerosols (SOA) are formed when VOC's are oxidized in the atmosphere, creating semivolatile products that partition from the gas to the aerosol phase. The aerosol yield Y is defined as:

$$Y = \frac{SOA(formed)}{VOC(consumed)}$$

The aerosol yield in the original MAPS model is a constant. Several recent studies have demonstrated that Y depends on temperature and the amount of organic matter present (M_O):

$$Y = M_0 \sum_i \frac{\alpha_i K_i}{1 + K_i M_0}$$

Here α_i is the individual formation yield for oxidation product *i* and K_i is the corresponding absorption equilibrium constant.

The temperature dependence of K_i can be expressed as:

$$K_i(T) = K_i \cdot \frac{T}{T_{ref}} \cdot EXP\left[\frac{H}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right]$$

where T_{ref} is a reference temperature (e.g. 303K), R is the ideal gas constant (0.0019872 kcal/mol K) and H is the enthalpy of vaporization.

Results

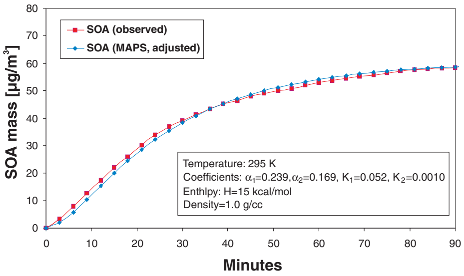

Figure 1: *Gas chamber experiment from Stanier and Pandis (2002) at 295 K, where 400 ppb ozone is mixed with 73 ppb α-pinene (with 2-butanol as OH scavenger). The aerosol mass formed during the experiment is compared to SOA concentrations calculated from MAPS with inclusion of new partition coefficients.*

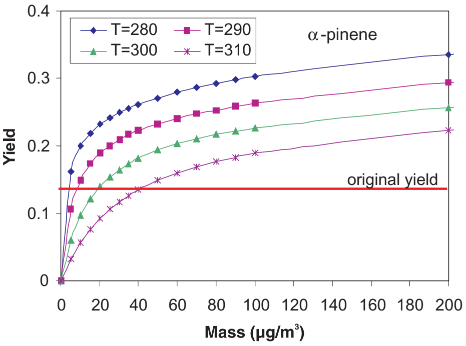

Figure 2: *Temperature dependent partition functions for α-pinene reactions with O_3. The following coefficients are used: α_1=0.239, α_2=0.169, K_1=0.052, K_2=0.0010, H=15 kcal/mol, and T_{ref}=303K.*

References

Kumar N., Lurmann F. W., and Carter W. P. L. (1995). Development of the flexible chemical mechanism version of the urban airshed model. Final report prepared for the California Air Resources Board, Sacramento, CA by Sonoma Technology, Inc., Santa Rosa, CA, STI-94470-1508-FR, August.

Stanier, C. O., and S. N. Pandis (2002). Secondary organic aerosols: Laboratory results for gas-aerosol partitioning and its dependence on temperature and relative humidity, *Aerosol Conference in Taiwan*, September 2002.

Takekawa H., H. Minoura, S.Yamazaki (2003). Temperature dependence of secondary organic aerosol formation by photo-oxidation of hydrocarbons, *Atmos. Env.*, 37 (24), 3413-3424.

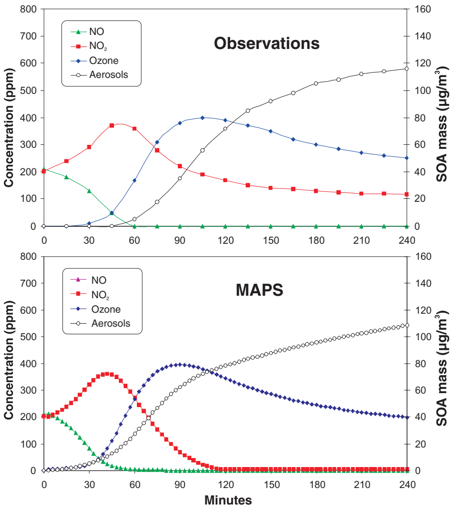

Figure 3: *Gas chamber experiment from Takekawa et al. (2003) where 4.33 ppm toluene, 0.211 ppm NO, 0.202 ppm NO_2, and 0.9 ppm propene are mixed and irradiated by black lights. The upper panel represent observed values, whereas the lower panel is modelled gas and aerosol concentrations with inclusion of the partition function shown in Figure 4.*

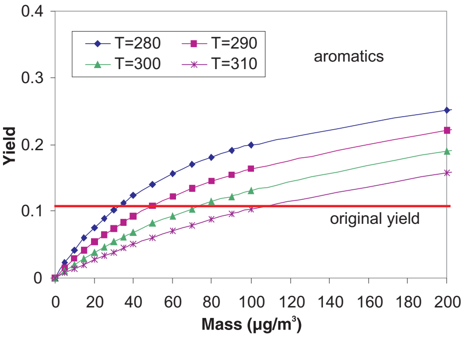

Figure 4: *Temperature dependent partition function for toluene reactions with OH (based on experiments from Takekawa et al., 2003). Partition coefficients: α_1=0.340, K_1=0.0057, H=7.4 kcal/mol, and T_{ref}=303K.*

Conclusion

SOA concentrations measured from the gas chamber experiments seem to agree fairly well with aerosol formations calculated from MAPS with adoption of the new partition functions. However, most experiments are performed at high temperatures and more model testing needs to be done for lower temperatures.

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