A Study of Cloud Processing of Organic Aerosols Using Models and CHAPS Data

Summary

The main theme of our work has been the identification of parameters that mostly affect the formation and modification of aerosol particles and their interaction with water vapor. Our detailed process model studies led to simplifications/parameterizations of these effects that bridge detailed aerosol information from laboratory and field studies and the need for computationally efficient expressions in complex atmospheric models.

One focus of our studies has been organic aerosol mass that is formed in the atmosphere by physical and/or chemical processes (secondary organic aerosol, SOA) and represents a large fraction of atmospheric particulate matter. Most current models only describe SOA formation by condensation of low volatility (or semivolatile) gas phase products and neglect processes in the aqueous phase of particles or cloud droplets that differently affect aerosol size and vertical distribution and chemical composition (hygroscopicity). We developed and applied models of aqueous phase SOA formation in cloud droplets and aerosol particles (aqSOA). Placing our model results into the context of laboratory, model and field studies suggests a potentially significant contribution of aqSOA to the global organic mass loading.

The second focus of our work has been the analysis of ambient data of particles that might act as cloud condensation nuclei (CCN) at different locations and emission scenarios. Our model studies showed that the description of particle chemical composition and mixing state can often be greatly simplified, in particular in aged aerosol. While over the past years many CCN studies have been successful performed by using such simplified composition/mixing state assumptions, much more uncertainty exists in aerosol-cloud interactions in cold clouds (ice or mixed-phase). Therefore we extended our parcel model that describes warm cloud formation by ice microphysics and explored microphysical parameters that determine the phase state and lifetime of Arctic mixed-phase clouds.

Results

a) SOA formation

Cloud droplets represent an aqueous medium where unique chemical processes can occur. Many recent laboratory studies provide detailed mechanistic information on chemical processes that lead to organic mass formation in droplets. We have shown that the mass yield of such processes can be reduced to simple expressions that describe cloud aqSOA formation as a function of cloud properties (liquid water content, lifetime) and chemical conditions (aqSOA precursor concentrations) (Ervens et al., 2008). While cloud droplets comprise a relatively dilute aqueous phase (milli-micromolar), the aqueous volume of aerosol particles is much smaller (by 3-5 orders of magnitude) but much more highly concentrated in terms of solutes (~ molar). This higher abundance of solutes facilitates chemical reactions that form unique products, such

macromolecular products, and oligomers. Based on laboratory studies, we have derived reaction parameters that describe the uptake and processing of a proxy organic compound (glyoxal) in aerosol water which leads to the formation of organic compounds similar to those as identified in ambient aerosol particles but whose sources could not be explained by previous SOA models (e.g., macromolecular compounds) (Ervens and Volkamer, 2010).

A comprehensive review of laboratory, field and model studies highlights that aqSOA formation in clouds and aqueous particles might be equally efficient in terms of mass production and that these processes together might be ubiquitous and significantly contribute to global organic aerosol loading (Ervens et al., 2011a). In addition, the application of our models to ambient data sets acquired during targeted field studies revealed that (i) precursors of cloud aqSOA might be efficiently formed upon ocean emissions (Rinaldi et al., 2011), and (ii) the aqueous phase of clouds and fog might act as a reservoir of carcinogen nitrosamines (Hutchings et al., 2010).

At low relative humidity and cloudiness, observed organic aerosol mass can be comprehensively explained by traditional approaches, i.e. by the oxidation of biogenic and anthropogenic precursors and subsequent condensation on preexisting aerosol (Bahreini et al., 2009).

b) Cloud condensation nuclei (CCN)

The conclusions in the literature about the importance of detailed representation of its physico-chemical properties of the organic aerosol fraction for successful prediction of CCN number concentration are ambiguous. Several CCN studies report that for aerosols close to emission sources, the mixing state has to be taken into account since freshly emitted hydrocarbon-like particles are hydrophobic and externally mixed (i.e. form a separate population), and, thus do not act as CCN. Other studies claim that at any location details of the chemical composition (size-resolved composition, organic properties …) are essential to obtain good closure.

The findings in previous studies are usually based on a single data set. In order to assess the importance of composition and mixing state for CCN prediction in a more general way, we have analyzed CCN measurements at locations that differ by types of and distance to emission sources (Riverside, CA; Mexico City; Houston Ship Channel and Gulf Coast; Point Reyes; Holme Moss, UK and Chebogue Point). We made simplified assumptions of the mixing state (internal/external) and composition (soluble/insoluble) of the organic fraction and could show that within relatively short temporal (few hours) and spatial (~ 10 km) scale organics appear to be soluble and internally mixed with other aerosol constituents. In addition, we explored the extent to which uncertainties in CCN number concentrations translate into differences in predicted cloud drop number concentration, which is ultimately the parameter of interest for aerosol/cloud interactions (aerosol indirect effect). In agreement with prior studies we showed that only at very low updraft velocities, the difference in CCN closure leads to the same error in droplet closure while at higher updraft velocities these errors are significantly reduced (Ervens et al., 2010).

c) Ice nucleation

While we have shown that the activation of particles into cloud droplets in warm clouds is only a weak function of chemical composition, the role of physicochemical properties of ice nuclei (IN) is much more uncertain. These uncertainties imply that the fundamental physical processes that maintain supercooled liquid in observed mixed-phase clouds are poorly constrained. Such clouds have a large impact on radiative fluxes in the Arctic, a region that is highly sensitive to climate change.

A cloud parcel model that has been used previously to simulate warm cloud formation has been extended by a module that describes formation of ice particles by vapor condensation on IN (deposition freezing) and freezing of IN immersed in cloud droplets (immersion freezing) and the detailed description of ice habits. Model simulations were performed in order to isolate the factors that control ice/liquid partitioning during the ascent of an air parcel. We were able to show that for most conditions, ice and liquid coexist, and only at high IN concentrations or low updraft velocities, do ice particles grow at the expense of droplets and thus limit the cloud lifetime. The impact of the ice nucleation mode on ice/liquid distribution depends on the temperature and supersaturation regime. The assumption of spherical ice particles instead of non-spherical habits leads to an underestimate of ice growth. It is concluded that updraft velocity, IN concentrations, and particle shape can impact ice/liquid distribution to similar extents (Ervens et al., 2011b).

Deliverables

Peer-reviewed publications

Ervens, B., Carlton, A. G., Turpin, B. J., Altieri, K. E., Kreidenweis, S. M., and Feingold, G.: Secondary organic aerosol yields from cloud-processing of isoprene oxidation products, Geophys. Res. Lett., 35, 2,L02816, 10.1029/2007gl031828, 2008.

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Ervens, B., Turpin, B. J., and Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA): a review of laboratory, field and model studies, Atmos. Chem. Phys., 11, 21,11069–11102, doi:10.5194/acp-11-11069-2011, 2011a.

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Bahreini, R., Ervens, B., Middlebrook, A. M., Warneke, C., DeGouw, J. A., DeCarlo, P., Jimenez, J. L., Brock, C. A., Neuman, J. A., Ryerson, T. B., Stark, H., Atlas, E., Brioude, J., Fried, A., Holloway, J. S., Peischl, J., Richter, D., Walega, J., Weibring, P., Wollny, A. G., and Fehsenfeld, F. C.: Organic aerosol formation in urban and industrial plumes in Houston, TX, J. Geophys. Res., 114, D00F16,doi:10.1029/2008JD011493, 2009.

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Ervens, B., Feingold, G., Sulia, K., and Harrington, J.: The impact of microphysical parameters, ice nucleation mode, and habit growth on the ice/liquid partitioning in mixed-phase Arctic clouds, J. Geophys. Res., 116, D17,D17205, 10.1029/2011jd015729, 2011b.

Conference contributions

Ervens, B., R. Bahreini, and R. Volkamer, Recent developments in organic aerosol modeling, Department of Energy, Atmospheric Science Program (ASP), Annual meeting, Santa Fe, NM, **2009**.

Ervens, B., Organic aerosol formation in aqueous particles, Gordon Research Conference, Atmospheric Chemistry, Waterville Valley, NH, **2009.**

Ervens, B. and R. Volkamer, SOA formation in aqueous particles: a significant SOA source, International Aerosol Modeling Algorithms (IAMA) Conference, Davis, CA, USA, **2009**.

Ervens, B. and R. Volkamer, Modeling SOA formation in the aqueous phase - Comparing chemical processes in aqueous aerosol particles and cloud droplets, AGU Fall Meeting, San Francisco, CA, **2009.**

Ervens, B., G. Feingold, K. Sulia, J. Y Harrington, On the Role of Ice Formation Mechanisms and Habit Growth in the Maintenance of Mixed Phase Arctic Stratus, AGU Fall Meeting, San Francisco, CA, **2010**.

Ervens, B., Cubison M. J., Andrews, E. , Feingold G., Ogren J. A., Jimenez, J. L. , Quinn, P. K. , Bates, T. S., Wang, J., Zhang, Q., Coe, H., Flynn, M., Allan J. D., CCN predictions using simplified assumptions of organic aerosol composition and mixing state, Annual Meeting of the Atmospheric System Research Program (ASR), Department of Energy, Bethesda, MD, **2010**.

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Hutchings, J. W., B. Ervens, P. Herckes, Secondary organic aerosol formation through cloud processing of aromatic VOCs, AGU Fall Meeting, San Francisco, CA, **2010.**

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Ervens, B., Turpin, B. J., Weber, R. J.: Secondary organic aerosol formation in cloud droplets and aqueous particles (aqSOA) – a review, Gordon Research Conference, Atmospheric Chemistry, Mount Snow Resort, West Dover, VT, **2011.**

Ervens, B., and G. Feingold, The dependence of the active site distribution of heterogeneous IN on the phase partitioning in mixed-phase clouds, AGU Fall Meeting, San Francisco, CA, **2011.**

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Herckes, P., Ervens, B., Wang, Y., Eagar, J., Leaitch, R., Macdonald, A., Sjostedt, S., Abbatt, J., Cloud water measurements of glyoxal and methylglyoxal during the Whistler Aerosol and Cloud Study (WACS), AGU Fall Meeting, San Francisco, CA, **2011.**

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