CCN predictions using simplified assumptions of organic aerosol composition and mixing state

Barbara Ervens\textsuperscript{1,2}, M. J. Cubison\textsuperscript{3}, E. Andrews\textsuperscript{1,2}, G. Feingold\textsuperscript{4}, J. A. Ogren\textsuperscript{2}, J. L. Jimenez\textsuperscript{2,3}, P. K. Quinn\textsuperscript{4}, T. S. Bates\textsuperscript{4}, J. Wang\textsuperscript{4}, Q. Zhang\textsuperscript{4}, H. Coe\textsuperscript{7}, M. Flynn\textsuperscript{7}, J. D. Allan\textsuperscript{8}

barbara.ervens@noaa.gov

\textsuperscript{1} CRES, University of Colorado, Boulder, CO; \textsuperscript{2} NOAA, ESRL/CSD Boulder, CO; \textsuperscript{3} Dept. of Chemistry and Biochemistry, University of Colorado, Boulder, CO; \textsuperscript{4} NOAA Pacific Marine Environmental Laboratory, Seattle, WA; \textsuperscript{5} Brookhaven National Laboratory, Upton, NY; \textsuperscript{6} Department of Environmental Toxicology, University of California, Davis, CA; \textsuperscript{7} School of Earth, Atmospheric and Environmental Science, The University of Manchester, UK; \textsuperscript{8} National Centre for Atmospheric Science, School of Earth, Atmospheric & Environmental Sciences, The University of Manchester, Manchester, UK

\textbf{Introduction}

An accurate but simple quantification of the fraction of aerosol particles that can act as cloud condensation nuclei (CCN) is needed for implementation in large-scale models. Seven data sets on aerosol size distribution, chemical composition, and CCN concentration ($N_{CCN}$) have been analyzed to explore the extent to which simple assumptions of organic composition and mixing state can reproduce measured CCN number concentrations. In addition, effects of these assumptions on cloud drop number concentration ($N_d$) are investigated.

\textbf{Data Sets}

Data sets differ in distance from and nature of sources and pollution level.
- Riverside, CA (RVS)\textsuperscript{(*)}
- Point Reyes (PYE)\textsuperscript{(*)}
- Mexico City, TO (MEX)\textsuperscript{(*)}
- Holme Moss, UK (HOM)\textsuperscript{(*)}
- Houston Ship Channel (HSC)\textsuperscript{(*)}
- Chebogue Point (CBG)\textsuperscript{(*)}
- Houston Gulf Coast (HGC)\textsuperscript{(*)}

\textsuperscript{(*)} detailed CCN analysis in previous study

\textbf{CCN Model}

\textbf{Initialization}

- Measured size distributions
- $N_{CCN}$ at one supersaturation in the range 0.27% ≤ $S$ ≤ 0.44% (depending on data set); if available, temperature gradients in the in the CCN counter are taken into account.
- Aerosol composition:
  - SO$_2^+$, NO$_x^+$, NH$_4^+$, (Cl), organics (Aerosol mass spectrometer)
  - Black carbon (if available)
- Time-dependent bulk measurements; not size-resolved

\textbf{Assumptions of Organic Composition and Mixing State}

- Externally mixed, insoluble organics
- Externally mixed, soluble organics ($K_{org} = 0.12$)
- Internally mixed, insoluble organics
- Internally mixed, soluble organics ($K_{org} = 0.12$)

\textbf{References}

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\textbf{Effects on Cloud Drop Number Concentration}

\textbf{Cloud Model}

- The model describes the activation of an internally mixed aerosol population into cloud droplets in a constant updraft ($w$)
- A reference composition ($R$) is chosen that translates into a critical diameter $D_1$ (equilibrium diameter at $S = 0.3\%$; Köhler equation)
- In order to simulate an error of 2 in $N_{CCN}$ ($\Delta N_{CCN} = 100\%$), two ‘$R$, $K$’ pairs are defined ($D_05$, $\kappa_{05}$ and $D_2$, $\kappa_2$) that define 0.5·$N_{CCN}$ and 2·$N_{CCN}$ (Fig. 3)

\textbf{Results}

- At low $w$, the error in $N_d$ ($\Delta N_d$) can be as high as $\Delta N_{CCN}$ for high particle concentrations (‘polluted conditions’)
- At $w > ~100$ cm s$^{-1}$, $\Delta N_{CCN} \approx 100\%$ translates into $\Delta N_d \leq 20\%$ due to the relatively larger impact of $w$ on $S$ as compared to that of aerosol composition
- Errors are largest if the smallest activated particles are at the steepest part of the particle number concentration

\textbf{Conclusions}

- Close to pollution sources, complex composition and mixing state (size-resolved) assumptions need to be made in order to predict $N_{CCN}$
- Externally mixed, hydrophobic organic particles seem to be sufficiently processed by chemical/physical ageing within 10s km downwind of emission sources and can be represented as an internal mixture.
- Different composition/mixing state assumptions lead to similar $N_{CCN}$ as different subsets of the population are predicted to activate. Such compensating factors might lead to good CCN closure even though the assumed and actual composition/mixing state are not identical.
- $\Delta N_{CCN} = 100\%$ translates into $\Delta N_d \approx 15\%$ under most conditions which is relatively small compared to radiative forcing uncertainties associated with cloud fraction and depth.

\textbf{Figure 1:} CCN closure results as a function of distance from sources; symbol size: Frequency of this ratio ‘CCN$_{model}$/CCN$_{meas}$.’ in CCN closure
- Close to emission sources, particles are externally mixed. Assumption of bulk composition is not sufficient and size-resolved composition has to be taken into account (e.g., hydrophobic organics - 100 nm)
- ~10s km downwind of sources, particles are sufficiently mixed and the assumption of hygroscopic organics gives best closure

\textbf{Figure 2:} CCN closure results as a function of organic fraction
- $N_{CCN}$ are underestimated if organics are assumed insoluble at organic fractions > ~70%
- In all other cases, CCN number concentrations in aged aerosol are reproduced within a factor of 2

\textbf{Figure 3:} Size distributions: $D_05$ are critical diameters above which twice (half) as many particles are activated as compared to $D_1$

\textbf{Figure 4:} Effect of different compositions on $N_d$ as a function of $w$