Development and application of a hygroscopicity basis set for the analysis of the mixing state of nascent sea spray aerosols

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I. Background

Aerosol particles impact global climate directly through their interaction with incoming solar radiation, and indirectly by acting as cloud condensation nuclei (CCN). Because chemical composition affects their ability to act as CCN, particle-particle variability resultant of primary aerosol production is important for understanding the impact of aerosols on climate. Given the large coverage of the Earth’s surface by ocean systems, marine aerosols produced from breaking waves in the ocean are of specific interest.

This work presents a novel approach to characterizing complex aerosol populations by separating the “ambient” population into particle bins with representative cloud formation potential.

Here the cloud formation potential is measured as the single variable hygroscopicity parameter, kappa (κ), which quantifies the water uptake tendencies of aerosols from low (organic, hydrocarbons ~ 0.0) to high (inorganic, salts ~ 1.5). Total κ is calculated using the entire single average CCN data set, where a single average of κ values is calculated using the entire CCN data set.

Figure 1: Direct and Indirect Effect of aerosols on climate.

Figure 2: Particle-particle variability of marine aerosols impacts cloud formation potential.

II. Methods

One method for direct κ measurement is a size-resolved cloud condensation nuclei (SR-CCN) system.

Figure 3: (Left) SR-CCN schematic. (Right) SR-CCN activation curve for 50 nm artificial sea salt aerosol particles.

Particles are generated from one (internally-mixed) or multiple (externally-mixed) aqueous solutions with a constant output atomizer.

III. Research Questions

1. Can high resolution SR-CCN measurements be utilized to probe particle-particle variability in multiple component aerosol populations?
2. To what extent can theoretical model predictions of aerosol hygroscopicity be constrained with complex but representative laboratory experiments?

IV. Probing Aerosol Mixing State

For an internal aerosol mixture there is one activation sigmoid, corresponding to the single representative composition of all particles. The activation curve for an external mixture contains separate sigmoids, corresponding to the activation of each individual component.

The magnitude of each sigmoid is used to calculate the relative abundance of each component.

Figure 4: Mixing size prediction of κ for Internal Mixtures (Peters & Kinnekerwa, 2007).

V. Kappa Basis Set Analysis

This observed activation of individual components in a binary external mixture was expanded to a five-component system.

A model framework was developed where a combined fit was derived from the predicted activation of each known component.

The broader combined fit compared to pure compounds and internal mixtures indicates external mixing.

Figure 5: (Inlay) Relative abundance of each component at corresponding hygroscopicity (κ).

The multiple sigmoid framework has been generalized as a κ basis set model.

Normalized activation curves were integrated to calculate the relative abundance of particles in each prescribed hygroscopicity bin.

A distribution of κ values better characterizes particle diversity, where a single average κ-value calculated using the entire activation curve assumes internal mixing.

Figure 6: SR-CCN activation curves for 50 nm aerosol particles of sea salt (blue), dichloromethane salt, and 1:1 internal and external mixtures (gray and purple respectively).

VI. Environmental Impact

The impact of aerosol mixing state on cloud droplet activation is estimated by the following model system. In general, an external mixing assumption underestimates the number of CCN relative to an internal mixing assumption, with the two methods converging as supersaturation increases.

Figure 8: (Left) Ratio of the number of CCN calculated assuming external vs. internal mixing, and (Middle) the percent of particles activated in the external case as a function of supersaturation for the (Right) model aerosol populations with various prescribed hygroscopicity/mixing states.

The effect of accounting for external mixing on the number of CCN seems to be greatest for populations where some particles are highly hygroscopic and others are not. Moreover, this analysis suggests the largest impact occurs in clouds systems where the supersaturation remains below 0.5%.

VII. Application to Other Systems

The κ-basis set analysis developed here is fully generalizable, and can therefore be applied to any size-resolved CCN data set, such as this recent chamber study of limonene oxidation SOA products.

The κ-basis set analysis is well-suited for monitoring changes in particle mixing state as the experiment progresses, and is the next step for application of this technique to non-marine systems.

Figure 9: SR-CCN activation curves of limonene-extracted SOA under high and low-NH4 conditions at (Left) low and (Right) high relative humidity.

VIII. Conclusions

For additional details on this work: Schill et al. (2015) ACS Cent. Sci. A framework for the interpretation of SR-CCN activation curves that accounts for diversity in individual particle hygroscopcity, via a κ-basis set analysis, has been introduced.

Moreover, this technique is fully generalizable to any SR-CCN data set with sufficiently high supersaturation resolution, and can aid in the interpretation of low resolution data sets.

IX. Acknowledgements and References

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