DOE ASR funded

Laboratory Studies of Cloud Particle Formation, Mixing State, Physicochemical and Optical Properties of Carbonaceous Aerosols

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Introduction and Methods

The goal of our research is to reduce uncertainties in areas highlighted in the ASR Science and Program Plan by

(1) improving the understanding of aerosol and processes controlling atmospheric cloud and ice droplet formation (CCN = cloud condensation nuclei; IN = ice nuclei)

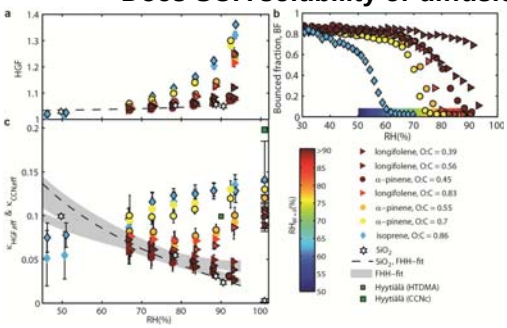
(2) improving the understanding and model representation of aerosol optical absorption/radiative transfer

(3) developing new integrated data sets combining multiple measurements to retrieve atmospheric aerosol properties

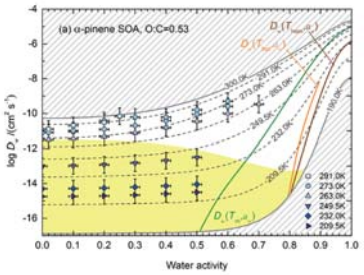
Our methods combine well-controlled laboratory generated carbonaceous particles (Secondary Organic Aerosol or SOA, black carbon soot, and SOA coated soot) with state-of-the-art instrumentation, developed in-house, or via joint experiments with local, national, and international collaborators.

Hygroscopicity and Cloud Formation

Does SOA solubility or diffusion control water uptake?



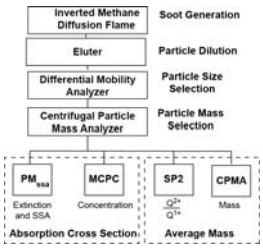
Panjunoja et al., 2015. Hygroscopic behavior of lab-generated SOA described using HTDMA, CCNc and ABI measurements. (a) Measured HGFs and (b) bounced fractions as a function of RH (c) Calculated hygroscopicity parameters (i.e., kappa's). Observations suggests that SOA phase (i.e., slightly soluble) limits water uptake by adsorption at RH<100% and explain discrepancies in kappa's measured for RH<100% and RH>100%. These differences could be atmospherically important.



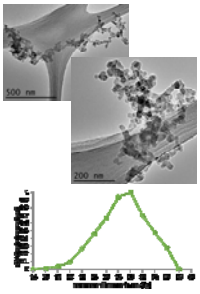
Lienhard et al., 2015. Water diffusion coefficients derived from kinetic response experiments of 25 micron particles of α-pinene SOA O:C=0.53, H:C=1.50 as a function of temperature. The dashed lines are temperature and composition dependent fits and the yellow areas mark regions where the mixtures are predicted to be in the glassy state. Observations suggest that water uptake is diffusion limited, and yet rapid enough to equilibrate under atmospheric conditions, indicating that diffusion is in most cases not likely to a limiting factor in cloud formation.

Black carbon physical, chemical and optical properties

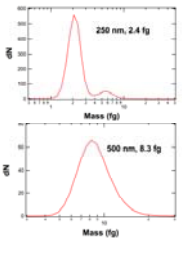
How well can we generate, measure, and predict black carbon physical, chemical, and optical properties?



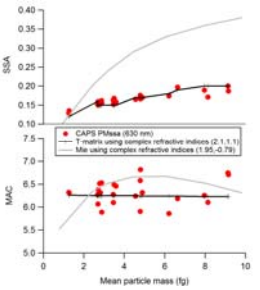
Laboratory generated inverted diffusion methane flame soot can be produced over a range of overall equivalence ratios (i.e., fuel-to-air), which control the size and 'maturity' of black carbon soot.



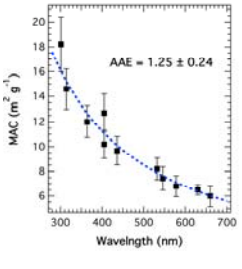
Size and mass selected soot (300 nm mobility diameter; 3.3 fg/particle). Overall equivalence ratio 0.7; 'mature' soot. TEM images showing diversity in shapes and derived primary spherule size distributions.



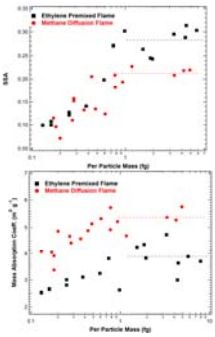
Even with mobility and mass selected soot, the SP2 measures multiply charged particles, which become large (>40%) at small sizes and must be taken into account for optical measurements.



Plot of measured SSA (top) and MAC (bottom) versus mean particle mass. Predictive theories (Mie and T-matrix) shown for two different complex refractive indices (Bond and Bergstrom and best fit). Mie can approximate MAC, but cannot predict SSA (i.e., scattering) correctly.



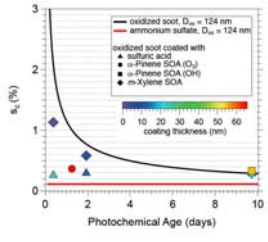
Wavelength-dependent absorption, measured using CAPS PMssa (630nm), UC Davis PAS (405 and 532nm) and UGA UV-Vis Absorption Spectrophotometer (301, 314, 364, 405, 436, 546, 578, 687 nm)



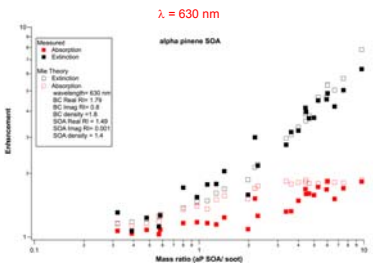
Changing the flame, fuel, or flame conditions can cause the resulting soot to become more 'immature', exhibiting higher SSA's and lower MAC's.

Coated black carbon CCN, optical properties and mixing state

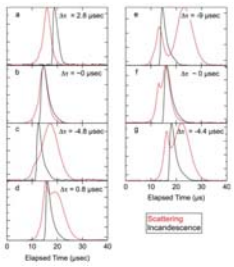
How does atmospheric aging affect black carbon?



Lambe et al., 2015. SOA coatings on black carbon soot increase CCN activation. Measured CCN critical supersaturation (Sc) as a function of photochemical age for oxidized soot particles with initial volume equivalent diameter Dve = 124 nm coated by sulfuric acid or SOA.



Coating black carbon particles with secondary organic (a-pinene and naphthalene SOA) and inorganic (sulfuric acid) aerosol dramatically affects scattering. Core-shell Mie models predict both reasonably well for significant condensed phase mass of SOA; however, discrepancies are evident for small coating thicknesses.



Sedlacek et al. 2015. Measuring the mixing state of atmospheric aerosol is extremely difficult. Here we explore the capabilities of the DMT SP2 instrument to measure internal mixing states of coagulated individual carbon black and solid sodium chloride particles (a–e) and carbon black and dioctylsebacate oil droplets (f,g) particles.

Acknowledge DOE ARM SP2

Summary

- Hygroscopicity of SOA particles, and therefore their optical properties and their cloud formation potential, may be controlled by the phase state of the particles and/or the diffusion of water through the particles.
- Recent developments in laboratory generation and characterization of black carbon particles can provide more accurate measurements and insights into black carbon particle physical, chemical, and optical properties and how to best predictively represent these in climate models.
- CCN activity, scattering, and absorption increase significantly for SOA coated black carbon particles. New single particle techniques and analyses are required to measure particle mixing states in ambient.

Collaborators: Virtanen et al. University of Eastern Finland; Kulmala et al. University of Helsinki; Donahue et al. Carnegie Mellon University; Riipinen et al. Stockholm University; Peter et al. ETH Zurich; Reid et al. University of Bristol; Koop et al. Bielefeld University; Rudich et al. Weizmann Institute; Sedlacek and Lewis Brookhaven National Laboratory; Chhabra Perkin Elmer; Trimborn Aeromegt GmbH; Mensah et al., ETH Zurich; Marr et al. Virginia Tech; Kroll et al. MIT; Cappa et al. UCDavis; Smith et al. UGA.

References: Pajunoja *et al.*, *Geophys. Res. Lett.* **42**, 3063–3068 (2015); Lienhard *et al.*, *Atmos. Chem. Phys.* **15**, 13599–13613 (2015); Chhabra *et al.*, *Atmos. Meas. Tech.* **8**, 1–18 (2015); Onasch *et al.*, *Aerosol Sci. Technol.* **49**, 409–422 (2015); Lambe *et al.*, *J. Aerosol Sci.* **79**, 31–39 (2015); Lambe *et al.*, *Atmos. Chem. Phys.* **15**, 3063–3075 (2015); Sedlacek *et al.*, *Aerosol Sci. Technol.* **49**, 872–885 (2015).