Measuring aqueous-phase browning in evaporating droplets: Aldehyde – amine reactions and cloud processing

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Aqueous-phase reactions likely occur in the atmosphere between small aldehydes, ammonium sulfate (AS), and amines [1]. Both aldol and imine oligomer products [2], along with light-absorbing brown carbon species [3], can be produced. While the initial steps of these reactions can take many hours in bulk solution [4], they can occur within seconds in drying droplets [5] – fast enough to trap organic material in a residual aerosol particle [6]. This accelerated loss of reactant species occurs because the evaporation of water increases their concentration and also reverses the hydration of reactive carbonyl functional groups. In this study, we examine whether brown carbon formation from aldehyde / amine / AS mixtures is also accelerated in drying droplets relative to bulk aqueous phase experiments. Cavity attenuated phase shift single scattering albedo (CAPS-ssa) measurements at 450 nm wavelength are used to probe the absorbance of lab-generated aerosol particles generated from the evaporation of aqueous droplets. Initial results suggest that browning at 450 nm is not accelerated by droplet evaporation to the same extent as reactant losses, possibly due to evaporation of key intermediates required to produce oligomers with systems of conjugated pi-bonds that are extensive enough to absorb visible light. This highlights the difficulty of extrapolating aqueous-phase processes observed in bulk-phase experiments to atmospheric conditions in cloud droplets and aqueous aerosol particles, where surface processes can play a much larger role.

[1] McNeill (2015), *Environ. Sci. Technol.* 49, 1237–1244. [2] Noziere & Cordova (2008), *J. Phys. Chem.* 112, 2827-2837. Galloway *et al.* (2009), *Atmos. Chem. Phys.* 9, 3331-3345. [3] Shapiro *et al.* (2009), *Atmos. Chem. Phys.* 9, 2289-2300. [4] Sedehi *et al.* (2013), *Atmos. Environ.* 77, 656-663. [5] De Haan *et al.* (2009), *Environ. Sci. Technol.* 43, 2818-2824. [6] Galloway *et al.* (2014), *Environ. Sci. Technol.* 48, 14417-14425.