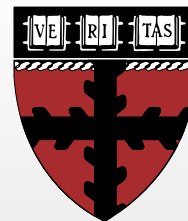


Highly Viscous States Affect the Browning of Atmospheric Organic Particulate Matter



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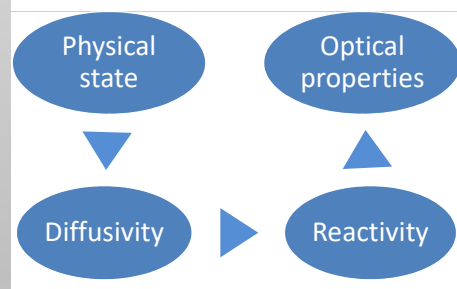
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Introduction

Light-absorbing organic carbon is of great interest because it potentially affects climate and photochemistry. Some types of secondary organic material (SOM) can become light-absorbing via multiphase reactive processing in the atmosphere, and thereby contribute to so-called “brown carbon” (Updyke et al. 2012). These multiphase browning reactions, however, can possibly be limited by the slow diffusion of reactant molecules in organic matrix under conditions that semisolids or solids prevail (Kuwata & Martin. 2012; Li et al., 2015).

Abstract:

Initially transparent organic particulate matter (PM) can become shades of light-absorbing brown via particle-phase reactions. When semisolid or solid physical states of organic PM prevail, however, the diffusion of reactant molecules can become sufficiently slow to inhibit browning reactions. Experiments show that the production of light-absorbing organonitrogen species from ammonia exposure strongly depended on the RH value. The observed RH-dependent behavior was well captured by a model that considered the diffusivities of both the large molecules making up the organic PM and the small reactant guest molecules taken up by the PM.



Experimental

- Organic particles were produced by photooxidation of toluene in an Oxidation Flow Reactor (OFR) (Kang et al. 2007; Lambe et al. 2011);
- In-particle diffusivities of both small (water) and large (organic) molecules were measured by a Quartz Crystal Microbalance (QCM);
- Toluene-derived SOM particles were exposed to ammonia;
- Organonitrogen species ($C_3H_7N_2^+$) were analyzed by the AMS
- Absorption spectra before and after ammonia exposure were recorded by a UV-VIS spectrometer.

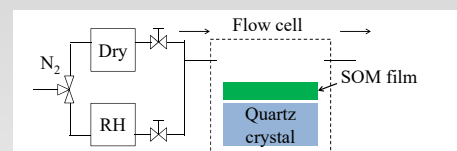


Figure 1. Diagram of the experimental apparatus for diffusivity measurements

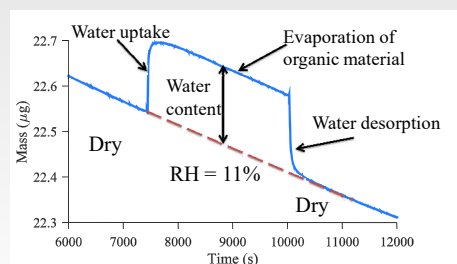


Figure 2. Illustration of QCM analysis (data shown for an α -pinene-derived thin film)

Diffusivities

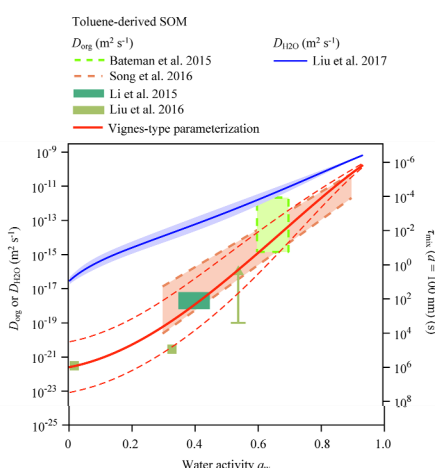


Figure 3. (left axis) Self-diffusivity D_{org} and water diffusivity D_{H_2O} for toluene-derived SOM; (right axis) mixing timescale for a 100-nm particle.

Organonitrogen

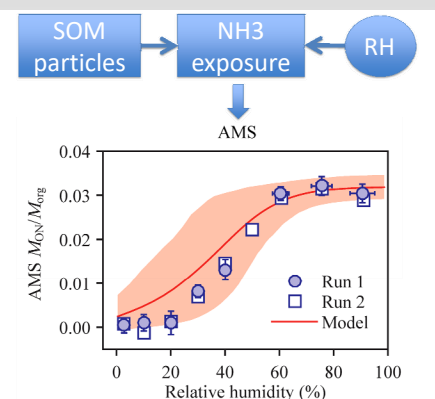


Figure 4. Organonitrogen production of toluene-derived SOM exposed to ammonia at different RH values. The red curve represents model results based on obtained diffusivities (Fig. 3). Water diffusivity was taken as a surrogate for NH_3 diffusivity.

Optical properties

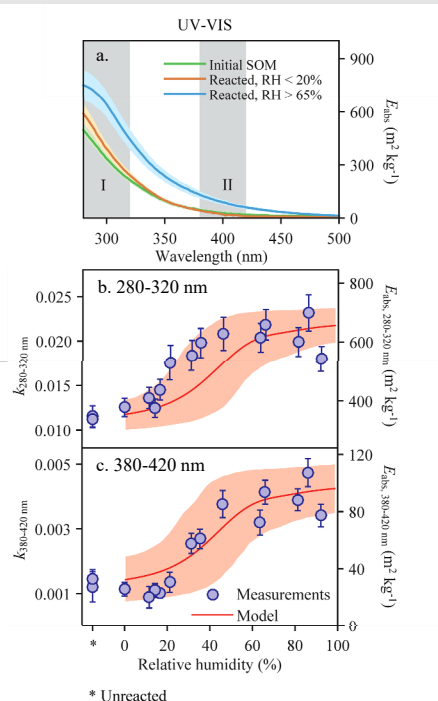


Figure 5. Changed optical properties of toluene-derived SOM exposed to ammonia at different RH values. (a) Mass absorption coefficient as a function of wavelength; (b) Absorptive indices on left axis and mass absorption coefficients on right axis from 280 to 320 nm (c) Same as panel (b) but for 380 to 420 nm

Conclusions

- Below 20% RH, fast browning reactions associated with ammonia uptake were kinetically limited by a shallow diffusoreactive length, even as the comparative physical mixing timescale of small molecules was short.
- Self-diffusivity of large organic molecules making up PM was 10^4 to 10^6 times smaller than the small-molecule diffusivity, further inhibiting reactant refreshing near the particle surface.

References

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