



Tracking the morphology of fulvic acids during water uptake

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Atmospheric humic like substances (HULIS) denote a range of oxidized, polyfunctional organic aerosol components widespread in the atmosphere, which show similar extraction behaviour on exchange columns as humic substances. Stemming from oxidation of primary gas phase and particulate organics, from e.g. biomass burning events, the HULIS constitute to a major fraction of the water soluble organic aerosol components in the atmosphere. Highly oxidized organic compounds play an important role in atmospheric processes like cloud formation or modification. Important factors therein are their hygroscopic properties and their microstructure, which influences their optical properties.

HULIS somewhat resemble humic substances from terrestrial and aquatic sources, which consist mainly of carboxylic, aromatic and phenolic moieties assembled into hydrogen and van der Waals bonded supermolecular structures. Hence, the Suwannee River fulvic acid (SRFA), a chemically well characterized fulvic acid obtained from the International Humic Substances Society, was used to obtain combined data on hygroscopic properties and microstructural evolution during water uptake.

The measurements were performed using x-ray absorption spectroscopy (NEXAFS, near edge x-ray absorption fine structure) in combination with an x-ray microscope (STXM, scanning x-ray transmission microscope) with a spatial resolution of about 30 nm. The measurements were performed at the PolLux beamline (SLS, Paul Scherrer Institut). The NEXAFS spectroscopy provides the possibility to map important chemical functional groups of carbon (as the one mentioned above) and oxygen atoms, and also to quantify the amount of carbon and oxygen atoms.

To follow the submicron structure during water uptake a new device – a microreactor – was developed for the STXM. Using this reactor, the samples could be kept in a microenvironment with controlled temperature and humidity from 0 to 95 %. The samples were deposited either as droplets with a microdispenser or as aerosol particles on the sample holder of the microreactor. The resulting dry droplet residues reached a size of about 20–30 μm or around 0.5 μm , respectively.

Using this setup we could obtain unique images showing the microstructure of the fulvic acid before and during exposure to water vapor *in situ*. Significant changes in morphology occurred upon water uptake, and the system consisted of a solution with embedded micron-sized colloidal particles. This further allows linking the chemical functional groups with their degree of hydration.

Additional measurements were performed with two fractionated fulvic acids of low (0.5-1 kDa) and high (10-30 kDa) molecular weight. Both fractions were first analyzed for their functional and their hygroscopic properties. Although the functional group analysis shows differences, the morphology of these two fractions was found to be similar. Under dry conditions, the residues were more homogeneous over the droplet dimensions than for the unfractionated samples. Under wet conditions, the two fractions differed in the amount of water taken up but were similar in the degree to which more phenolic subunits were apparent.