Aging and condensed phase chemistry affects the hygroscopicity of ambient SOA

A.L. Vogel[1,*], C. Müller-Tautges[1], M.L. Krüger[2], D. Rose[2,○], J. Schneider[3], G.J. Phillips[4,◊], U. Makkonen[5], H. Hakola[5], J.N. Crowley[4], U. Pöschl[2], and T. Hoffmann[1]

[1]Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, 55128, Germany
[2]Multiphase Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany
[3]Particle Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany
[4]Atmospheric Chemistry Department, Max Planck Institute for Chemistry, Mainz, 55128, Germany
[5]Finnish Meteorological Institute, Helsinki, 00560, Finland
*now at: CERN, European Centre for Nuclear Research, Geneva, 1211, Switzerland
[○]now at: Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt/Main, Germany
[◊]now at: Department of Natural Sciences, University of Chester, Chester, UK

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Presenting author email: alex.vogel@cern.ch

Secondary inorganic and organic aerosol particles are ubiquitous constituents in the atmosphere. They are largely produced through the photo-oxidation of gaseous precursor molecules, such as SO_2, NO_x and VOCs, from both anthropogenic and natural sources. Once grown to atmospherically relevant sizes, they can act as cloud condensation nuclei (CCN) and thus affect earth's climate (IPCC, 2013). However, their chemical composition can vary considerably over their atmospheric lifetime (up to one week) as a result of which, their physico-chemical properties may change significantly due to chemical transformation processes (Jimenez *et al.*, 2009). One of these properties is hygroscopicity, which largely depends on the chemical composition. Linking both, measured chemical composition and hygroscopicity helps to advance our current understanding of the hygroscopicity parametrisation.

In this work we investigated how photochemical aging of the organic aerosol fraction and chemical reactions between inorganic and organic compounds can affect the hygroscopicity parameter κ (Petters and Kreidenweis, 2007). The measurements were conducted at the semi-rural Taunus Observatory/ Germany during summer 2012. An extensive suite of particle phase characterizing instrumentation was applied for the detailed composition analysis of submicron aerosol: We used online atmospheric pressure chemical ionization mass spectrometry (APCI-MS) (Vogel *et al.*, 2013), aerosol mass spectrometry (AMS), and filter sampling for laboratory based analysis using ultrahigh performance liquid chromatography coupled to electrospray ionization ultrahigh resolution (Orbitrap^{TM}) mass spectrometry (UHPLC/ESI-UHRMS). The AMS allows quantification of total organics, sulfate and nitrate, whereas the APCI-MS can identify single organic species (organic acids, organosulfates, nitrooxy-organosulfates), both at a high measurement frequencies (< 1 minute). The UHPLC/ESI-UHRMS analysis of filter samples provides vital information helping to understand the complex online spectra of the APCI-MS by the unambiguous determination of the elemental composition of different organic compounds. Furthermore, we used a MARGA (Monitor for Aerosols and Gases in Ambient Air) to measure the concentration of purely inorganic sulfate in PM10. Finally a CCN counter coupled to a differential mobility analyser (DMA) and to a condensation particle counter (CPC) was used to measure size-resolved CCN efficiency spectra and to derive the hygroscopicity parameter κ.

We determined the κ-value of the ambient aerosol from size resolved chemical composition measurements by the AMS and compared it to the measured values of the CCN efficiency spectra. The relative evolution of the aerosol aging was determined by measuring the ratio of two biogenic acids: the aging product 1,2,3-methyl-butane-tricarboxylic acid (MBTCA) and the first generation oxidation product pinic acid by the online APCI-MS. The occurrence of organosulfates and nitrooxy-organosulfates was observed by the ultrahigh resolution MS analysis and the online APCI-MS. Comparison of the total sulfate concentration measured by the AMS with the sulfate measurements by the MARGA allowed for the determination of the fraction of sulfate which is bonded to organic molecules. We observed that photochemical aging and the formation of (hydrophobic) nitrooxy-organosulfates is responsible for the observed bias between the predicted and measured κ-value.

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