



Quantification of known and unknown biogenic organosulfates in summertime PM10 from Germany and China

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Organosulfates (OS) are ubiquitously abundant in atmospheric aerosol particles and known to be formed from reactions between reactive organic compounds and acidic sulfate aerosol. Nonetheless, the exact sources, formation mechanisms and the amount of OS in ambient aerosol are still unclear. In particular, uncertainties in total concentrations of OS are commonly due to a combination of a lack of authentic standards and the presence of unknown and yet unidentified OS.

Here we quantify known and unknown mono- and sesquiterpene-derived OS in summertime PM10 collected in field studies in rural Germany (Melpitz) and urban China (Beijing). We apply a non-target and a suspect analysis approach using liquid chromatography in combination with high-resolution Orbitrap mass spectrometry in different scan modes (i.e. full scan, data-dependent MS/MS, all-ion-fragmentation). Suspect monoterpene-derived OS (MT-OS) and sesquiterpene-derived OS (ST-OS) are identified 1) by their characteristic HSO₄⁻ fragment in all-ion-fragmentation mode, 2) their absence of aromaticity, and 3) a C₉–10 and C₁₄–15 carbon skeleton for MT-OS and ST-OS, respectively. Assuming similar ionization efficiencies among the different MT-OS and ST-OS, quantification is then carried out using a variety of authentic MT-OS and ST-OS standards. In addition, data from full scan and data-dependent MS/MS experiments are analyzed in an untargeted approach to obtain a more general characterization of the chemical composition of the aerosol samples.

Despite the quite different environments, i.e. rural background versus urban megacity, we find surprising similarities between the two sites. For both sites, we find about 50 MT-OS, although merely 13 of them are identical (i.e. exhibiting equal retention times, m/z ratios, and isotopic patterns). Moreover, total concentrations of MT-OS are in a similar range of 10–40 ng m⁻³. In both cases, MT-OS correlate significantly with particulate ammonium and sulfate, indicating that lower pH values and the presence of sulfate promote MT-OS formation. Remarkably, concentrations of common monoterpene oxidation products are significantly lower in Beijing samples, suggesting also other volatile organic compounds to serve as source for compounds resembling MT-OS.

In contrast to the similarities for MT-OS, number and concentration of ST-OS exhibit larger differences for the two sites. While we find about 16 ST-OS in Melpitz samples, the total number of ST-OS is more than doubled for the Beijing samples (i.e. 41 ST-OS). Moreover, merely 4 of these ST-OS are detectable at both sites. Correspondingly, total concentrations of ST-OS are larger for Beijing samples (i.e. 2–22 ng m⁻³) and lower for Melpitz samples (i.e. 0.5–5 ng m⁻³). While for Beijing we find a weak correlation for ST-OS concentrations and particulate ammonium, no such correlation is visible for Melpitz samples. Furthermore, for both sites no significant correlation of ST-OS to particulate sulfate is observable, possibly indicating long-range transport as source of ST-OS at both sites.