

Using Untargeted LC-HRMS/MS to Quantify Known and Unknown Terpenoid Organosulfates in PM₁₀ from Rural Germany and the North China Plain

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Organosulfates (OS) are a ubiquitous class of compounds in atmospheric aerosol particles formed by reactions between reactive organic compounds and acidic sulfate aerosol (Iinuma *et al.*, 2007, Surratt *et al.*, 2008). However, sources, formation mechanisms, and total amounts of OS in ambient aerosol are still connected to large uncertainties. In particular, a comprehensive molecular quantification of OS is commonly hampered because of missing authentic standards and the abundance of unknown and yet unidentified OS.

Here we quantified for the first time total concentrations of known and unknown monoterpene (MT) and sesquiterpene (ST) OS in summertime PM₁₀ from field studies in rural Germany (MEL; Melpitz, May 2014) and the North China Plain (NCP; Wangdu, June 2014). Using a combined targeted/untargeted approach of state-of-the-art high-resolution Orbitrap mass spectrometry (HRMS) coupled to liquid chromatography (LC); we found significant MT-OS and ST-OS concentrations at both sites. Data from full scan, data-dependent MS/MS, and all-ion-fragmentation experiments were analyzed in a non-target screening to obtain a general characterization of the chemical composition of the aerosol samples. Subsequent quantification of identified OS was carried out using a variety of authentic MT-OS and ST-OS standards.

At each site, we observed more than 50 MT-OS, 13 of which are detectable at both sites (i.e., consistent retention times, *m/z* ratios, and isotopic patterns). For both sampling locations, median concentrations of MT-OS were in the range of 10–40 ng m⁻³, to which the 13 common MT-OS contributed on average >55%. From all MT-OS, C₉H₁₆O₇S (MT-OS 267) was the main contributor with average mass concentrations of 2.23 and 6.38 ng m⁻³ for MEL and NCP, respectively. Given the pervasive abundance of MT-OS 267, the most likely source seemed to be limonene. In general, MT-OS concentrations correlated linearly with particulate ammonium and sulfate. However, only for MEL samples concentrations of MT-OS correlated with concentrations of well-known MT oxidation products (*R*²=0.72). In contrast, for NCP, rather low concentrations of MT oxidation products (i.e., typically <1 ng m⁻³) suggest a suppression of carboxylic acid formation under high levels of NO_x

and particulate sulfate, rather favoring the formation of N- and S- functionalized compounds such as OS.

Furthermore, we found significant differences in number and concentration of ST-OS at the sampling sites. While we observed 17 ST-OS for MEL samples, 40 ST-OS were detected in NCP samples. Moreover, merely five of these ST-OS were abundant at both sites. Correspondingly, total concentrations of ST-OS were larger for NCP (i.e., 2–22 ng m⁻³) and lower for MEL (i.e., 0.5–5 ng m⁻³), suggesting larger differences in particle chemistry and ST-OS formation. In particular, aerosol acidity was found to be key during ST-OS formation, and probably not sufficient in PM₁₀ from MEL, explaining the rather low ST-OS concentrations.

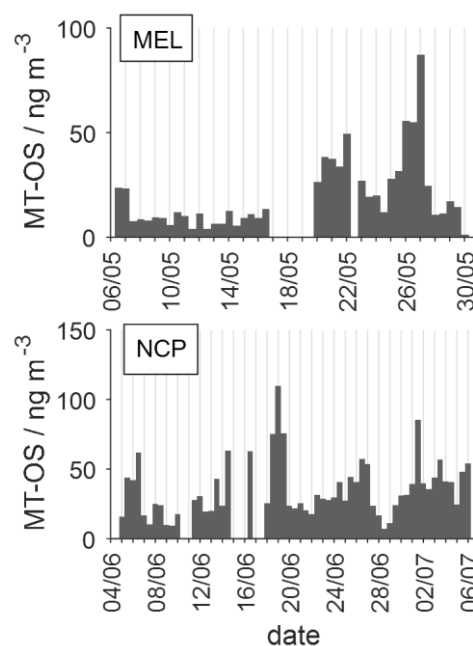


Figure 1. Total concentrations of MT-OS for MEL (upper panel) and NCP (lower panel) in PM₁₀.

Iinuma, Y., Müller, C., Böge, O., Gnauk, T., & Herrmann, H. (2007). *Atmos. Env.*, 41, 5571–5583.

Surratt, S., *et al.* (2008). *J. Phys. Chem. A*, 112, 8345–8378.