

# Real-time detection of highly oxidized organosulfates and SOA marker compounds during the F-BEACH 2014 field study

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The chemical composition of organic aerosols was analyzed using complementary mass spectrometric techniques during a field study in Central Europe in July 2014 (Fichtelgebirge – Biogenic Emission and Aerosol Chemistry, F-BEACH 2014). Aerosols were analyzed in real-time by techniques such as Aerosol Flowing Atmospheric-Pressure Afterglow Mass Spectrometry (AeroFAPA-MS) (Brüggemann *et al.*, 2015), Aerosol Mass Spectrometry (AMS), and Chemical Ionization Atmospheric-Pressure interface Time-of-Flight Mass Spectrometry (CI-APiToF-MS). In addition, offline detection of acidic organic compounds was conducted by non-target screening of filter samples using Ultra-High Resolution Mass Spectrometry (UHRMS).

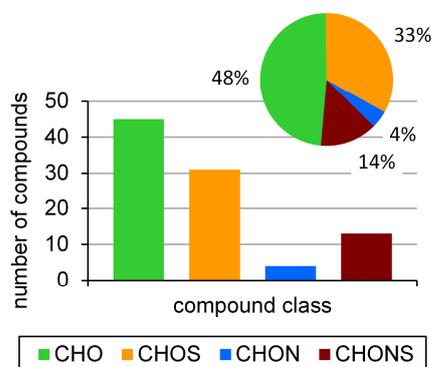


Figure 1. Number and ratio of identified compounds by LC-UHRMS analysis of filter sample extracts for each compound class.

In total, 93 acidic organic compounds were identified as major contributors to the organic aerosol mass at the site. Among the CHO-containing compounds several common biogenic secondary organic aerosol (BSOA) marker compounds were detected. High concentrations were found for the monoterpene photooxidation products 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) and 3-carboxyheptanedioic acid, suggesting that  $\alpha$ - $\beta$ -pinene and *d*-limonene oxidation products were dominating the organic aerosol fraction. In agreement, volatile organic compound (VOC) measurements showed high mixing

ratios for these monoterpenes in and above canopy level. Moreover, the high abundance of MBTCA and 3-carboxyheptanedioic acid and their concentration ratios to earlier-generation oxidation products, such as pinic acid, indicate that relatively aged aerosol masses were present during the campaign period. HYSPLIT trajectory calculations revealed that most of the arriving air masses traveled long distances (>1,500 km) over land under cloud-free conditions, further supporting this hypothesis.

Around 47% of the detected compounds from the filter sample analysis were sulfur-containing, suggesting a high anthropogenic impact on biogenic emissions and their oxidation processes. Among the sulfur-containing compounds, several organosulfates, nitroxy organosulfates, and highly oxidized organosulfates (HOOS) were unambiguously identified. In addition, correlations among HOOS classes, sulfate and highly oxidized multifunctional organic compounds (HOMs) were investigated. The results support the hypothesis of previous studies that HOOS are formed by reactions of gas-phase HOMs with particulate sulfate (Mutzel *et al.*, 2015). Furthermore, a good agreement was observed between HOOS formation and gas-phase peroxyradical ( $\text{RO}_2\cdot$ ) concentrations, suggesting  $\text{RO}_2\cdot$  to be either a direct or indirect precursor for HOOS. In addition, periods with high relative humidity revealed that aqueous-phase chemistry might play a major role in HOOS production.

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## References

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