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Chemical analysis of particulate and gaseous products from the monoterpene oxidation in the SAPHIR chamber during the EUCAARI campaign 2008

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The atmospheric oxidation of monoterpenes leads to multifunctional products with lower vapour pressure. These products condense and coagulate to existing particles leading to particle formation and growth.

In order to obtain better insights into the mechanisms and the importance of sources to organic aerosol, a mixture of monoterpenes was oxidised in the SAPHIR outdoor chamber during the EUCAARI campaign in 2008. The mixture was made of α-pinene, β-pinene, limonene, Δ3-carene and ocimene, representing a typical monoterpene emission from a boreal forest. In addition, two sesquiterpenes (α-farnesene and caryophyllene) were reacted together with the monoterpene mixture in some experiments. The VOC (volatile organic compound) mixture was reacted under tropospheric oxidation and light conditions in a prolonged time scale over two days.

In the present study, a special emphasis is put on the detection of carbonyl compounds from the off-line analysis of collected filter and denuder samples from the campaign in 2008. The oxidation products which contain carbonyl groups are important first stable intermediates during the monoterpene and sesquiterpene oxidation. They react further with atmospheric oxidants to form lower volatile acidic compounds, contributing to secondary organic aerosol (SOA).

Commonly used methods for the analysis of carbonyl compounds involve derivatisation steps prior to separation and subsequent UV or MS detection. In the present study, 2,4-dinitrophenylhydrazine (DNPH) was used to derivatise the extracted filter and denuder samples. The DNPH converts aldehyde- and keto-groups to stable hydrazones, which can be purified afterwards using a solid phase extraction (SPE) cartridge. The derivatised samples were analysed with HPLC/ESI-TOFMS which allowed us to determine the exact chemical formula of unknown products.

In addition to known carbonyl compounds from monoterpene oxidation such as pinonaldehyde and nopinon, previously unreported molecular masses were found. These were tentatively identified as hydroxycarbonyl compounds with the molecular weight of 168 ($C_{10}H_{16}O_2$) and 154 ($C_9H_{14}O_2$).