Formation of dimers of terpene oxidation products in relation to environmental parameters, *DIMERS*

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- Introduction and motivation

Organic condensable material is crucial for growth of aerosols from nucleation into larger size ranges of climatic relevance (e.g. Kulmala et al., 2013). Oxidation products of monoterpenes contribute to this growth, especially in the forest environment. We recently identified dimers of first-generation monoterpene oxidation products in atmospheric aerosols from Sierra Nevada Mountains, California (Kristensen et al., 2013) and Hyytiälä summer 2012 (previous TNA project). Dimers are of special interest due to their (expected) low volatility, compared to other terpene oxidation products, but their exact route of formation of dimers is still unresolved.

- Scientific objectives

The objective of this TNA was thus to obtain new knowledge on formation and occurrence of dimers of terpene oxidation products, and their role in particle formation and growth. There are only very few measurements of these dimers in ambient air, and from our previous TNA visit we know that the SMEAR II research station in Hyytiälä provides optimal conditions for such studies.
This study investigates variations in composition and concentration levels of terpene oxidation products, their dimers, as well as organosulfates in aerosol samples collected on a diurnal basis, and also at higher time-resolution during an intensive study period. This project will contribute to the understanding of processes affecting atmospheric aerosol growth, especially in a forest environment.

- Reason for choosing station

The SMR Station for Measuring Forest Ecosystem-Atmosphere Relations - SMEAR II provides an ideal location as the station is located in a rather homogenous Scots pine (Pinus sylvestris L.) stand on a flat terrain. The station thus represents boreal coniferous forest environment, and is well suited for studies of atmospheric chemistry of monoterpenes.
The station has top class instrumentation for measurements of aerosol microphysics, atmospheric chemistry, and micrometeorology and in this way we can have easy access to supplementary data which can help to understand and rationalize the results of our study. In addition the TNA took place during an intensive campaign period in connection with the PEGASOS project.

- Method and experimental set-up

We installed a high-volume (23.1 m^3/h) sampler with a PM_1 sampling inlet for collection of aerosols at SMEAR II. High-volume samples were collected automatically on a diurnal basis for most of the sampling period 1 May - 19 June 2013, except for an intensive study period (during the TNA) when 4-6 samples were collected per day. We successfully collected a total of 111 aerosol filter samples using the high-volume sampler. The samples were shipped to Aarhus at cold conditions.
Aerosol samples were extracted and analyzed at Aarhus University by ultrahigh performance liquid chromatography (UHPLC) quadrupole time-of-flight mass spectrometry. The method was based on the methodology of Kristensen and Glasius (2011) and Kristensen et al., 2013.

Data analysis and interpretation will benefit from the huge amount of data obtained from on-going and campaign measurements at SMEAR II.

- Preliminary results and conclusions

From the preliminary analysis we have identified several organic acids and organosulfates of both biogenic and anthropogenic origin in the samples, as well as three dimer esters from monoterpenes. The total air concentration of the identified compounds was 91± 71 ng/m^3 on average during the study period with pinic acid and pinonic acid being the dominating compounds, contributing 17±21 ng/m^3 and 39±40 ng/m^3, respectively. In general the organic acids were found at highest concentrations (82±66 ng/m^3) followed by the dimer esters (6±7 ng/m^3). The concentration of the organosulfates being very low (2±2 ng/m^3) with the monoterpene-derived organosulfates dominating.

No clear distinction was observed between night and day samples, but event periods with increased concentrations of specific compounds were identified. The connection between the event periods and meteorological parameters, as well as transport patterns of the air masses will be further investigated.

It is interesting to note the relatively high occurrence of dimer esters of monoterpene oxidation products at this site compared to levels in e.g. Denmark. Data analysis will focus on investigation of the reasons for this, as well as possible influence on particle processes.

- Outcome and future studies

The results of this work will improve knowledge on formation of dimer esters of monoterpene oxidation products, as well as environmental processes of relevance to formation and levels of carboxylic acids and organosulfates in the boreal forest environment. The outcome will be of importance to our understanding of processes contributing to aerosol formation and growth, especially in the boreal zone.

- References

K. Kristensen and M. Glasius (2011) Organosulfates and oxidation products from biogenic hydrocarbons in fine aerosols from a forest in North West Europe during spring. *Atmospheric Environment*, 45, 4546-4556.

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