

Measuring Organic Vapors In Nucleation and Growth (MOVING) using chemical ionization and aerosol mass spectrometry

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Introduction and motivation

Secondary organic aerosol (SOA) comprises a major fraction of submicron aerosols, which play a critical but still poorly understood role on climate forcing, human health, visibility, and acid deposition. These effects depend on aerosol composition, size, and geographic distribution. Over the last decade large gaps have been identified in comparisons between SOA models and measurements. However, there are still unanswered questions regarding the key sources and factors that control SOA formation in ambient air. New evidence (Ehn et al., 2014) strongly suggests that a potentially significant fraction of global SOA could be formed through the condensation of the oxidation products of biogenic volatile organic compounds (VOC). Thanks to the recent development of new capabilities for the measurement of these low volatility organic compounds, mainly via high resolution mass spectrometry (Junninen et al., 2010, Ehn et al., 2012), it is now understood that low volatility, organic condensable material is crucial for the growth of aerosols from nucleation into larger size ranges of climatic relevance (e.g. Riccobono et al., 2014). Oxidation products of monoterpenes contribute to this particle growth and SOA formation especially in forest environments, such as in Hyytiälä (e.g. Kulmala et al., 2013).

Scientific objectives

The deployment at the Hyttiala Forestry SMEAR II station proposed for April-May 2014 aimed to gain insights into the initial formation of particle clusters and the role of organic molecules for their growth into larger clusters and ultimately into secondary organic aerosols (SOA). Several chemical ionization mass spectrometers (CIMS) and aerosol instrumentation were deployed to connect the aerosol gaseous precursors to the aerosol particle physical and chemical properties. The CIMS provides high resolution measurements (including characterization at the molecular level and quantification) of organic molecules in the gas phase that are believed to be key for SOA formation. The particle size magnifier (PSM) is able to detect nano-sized condensation nuclei (nano-CN) as small as ~1 nm in mobility diameter, and to grow them to mean diameter of 90 nm, after which an ordinary condensation particle counter can be used to count the grown particles. Finally, the HR-AMS provides high resolution, sized resolved measurements of the chemical composition of sub-micron aerosol particles (organic and inorganic components). The deployment of such state-of-the-art instrumentation intended to elucidate the role of gaseous organic molecules for new particle formation (NPF) and growth into submicron SOA.

Reason for choosing station

The SMEAR II station (Station for Measuring Forest Ecosystem Atmosphere Relations) in Hyytiälä is an ideal location as it is located in a relatively remote area dominated by pine trees (*pinus sylvestris*), therefore representing a pristine boreal coniferous forest environment. Biogenic volatile organic compounds (BVOC), mainly monoterpenes, represent the majority of emissions at this location. Therefore, Hyytiälä has been chosen over the years as it is a "hot spot" for studying the chemistry of monoterpenes. The SMEAR II station in Hyytiälä is an excellent infrastructure with all the relevant auxiliary aerosol measurements. The station has top class instrumentation for continuous measurements of aerosol microphysics, atmospheric chemistry, and micrometeorology, which can be critical to help to understanding the results of our study.

Method and experimental set-up

The instruments deployed during the campaign were installed in several different containers. Several CIMS instruments running with different chemical ionization (CI) schemes were deployed to measure organic molecules over a wide range of oxidation levels. One of the trailer hosted an acetate (CH_3COO^-) CIMS (Veres et al., 2008) to measure oxidized organic molecules with $\text{O:C} < 1$ and two CIMS configured to measure sulfuric acid and peroxyradicals. Another atmospheric inlet pressure mass spectrometer (APi-ToF, Junninen et al., 2010) measured neutral clusters. A second trailer hosted several PSM instruments that were setup to measure nano clusters in different size ranges, and aerosol chemical speciation monitor, ACSM (Ng et al., 2012) to measure the composition of the bulk submicron aerosol. Finally, a third container hosted the an high resolution soot particle mass spectrometer equipped with a laser to detect refractory and non-refractory material, SP-AMS (Onasch et al., 2012) along with other particle instruments. All the trailer were provided with adequate inlet systems (include a cyclone impactor and / or drier for the particle measurements) to optimize the sampling of outside air.

Specifically to this TNA, we proposed to deploy a University of Helsinki (UHEL) nitrate ion (NO_3^-) based CIMS and a University of Washington (UW) iodide (I^-) CIMS equipped with a particle collector (basically a filter mounted on a teflon plate, called FIGAERO) to also measure the aerosol particle phase via thermal desorption, thereby providing high resolution measurements of both gas and particulate composition, with an emphasis on organic components over a wide O:C range. Both the UHEL NO_3^- (Ehn et al., 2012) and the UW I^- FIGAERO CIMS (Lopez-Hilfiker et al., 2014) were located on the tower, and were provided with a short inlet for limiting sample losses. The UW FIGAERO CIMS was housed within a weather-proof container (1.5 m x 1 m x 0.75 m). The sub-micron particle composition was analyzed by temperature programmed thermal desorption over alternating 45 minute periods.

Preliminary results and conclusions

The data collected with the Kuopio SP-AMS showed that the majority of the submicron PM was represented by organics (ORG). Average ORG loadings were 2 $\mu\text{g}/\text{m}^3$, but reached 10 $\mu\text{g}/\text{m}^3$ during some instances such as May 15-25 and June 1-10, likely due to polluted air masses coming from Northern Europe. During those times, sulfate (SO_4^{2-}) was also enhanced. The black carbon (BC) concentration was low during the campaign, (less than 0.5 $\mu\text{g}/\text{m}^3$) as expected given that the site is away from direct combustion sources. The connection between these events and meteorological parameters, as well as transport patterns of the air masses to Hyytiälä will be further investigated.

Outcome and future studies

The results of this work will improve knowledge on the monoterpene oxidation products, as well as environmental processes of relevance to formation of organic particles in the boreal forest. The outcome will be of importance to our understanding of processes contributing to the formation of organic aerosol in the boreal environment.

References

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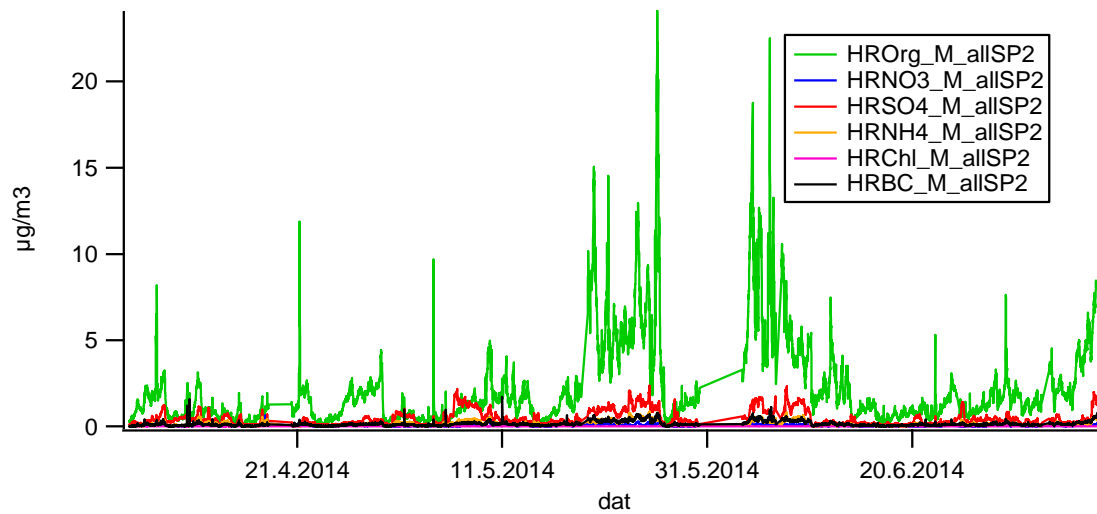


Figure: Time series of the refractory (BC) and non refractory (NR-PM, such as ORG, SO₄ etc.) components of the submicron PM as measured by the SP-AMS during April - May 2014 at th SMEAR II station in Hyttiälä.