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Changes in concentration of nitrogen-containing compounds in 10 nm particles of boreal forest atmosphere at snowmelt

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ABSTRACT

Measurements to clarify the chemical composition and especially the nitrogen compounds in 10 nm ultrafine aerosol particles were carried out at the boreal forest site at the SMEAR II station, Hyytiälä, Finland, during spring–summer–autumn of 2010 and in spring 2011. In 2011, laser aerosol mass spectrometer (laser AMS) provided in-situ chemical composition data for 10 nm particles. Laser AMS results, for samples collected in 2011, were clarified through comparison with findings for partly published 30 nm and all-sized particles from filter samples analyzed by chromatographic techniques, re-analysis of the selected 30 nm filter samples for quinoline identification by LC–MS and modified results from previously published atmospheric pressure interface time-of-flight mass spectrometer (APi-TOFMS) data. The chemistry of the atmosphere was found to change markedly in mid April 2011, just after snow melt: the concentrations of 35% of the laser AMS ions and compounds determined in 30 nm particles from filter samples clearly increased or decreased at this time. Notably, the amount of nitrogen compounds increased and the amount of aldehydes decreased. The laser AMS results for 10 nm aerosol samples demonstrated the tendency for nitrogen-containing compounds and oxygenated and non-oxygenated hydrocarbons to increase in concentration after snow melt. More detailed analysis confirmed that the two most interesting, frequently observed, and abundant laser AMS ions, m/z 143 and 185, originated from 1-(X-methylquinolin-X-yl) ethanone. According to laser AMS and APi-TOFMS data, when the quinoline concentrations in the 10 nm particulate phase increased, the concentrations in the molecular clusters decreased, indicating changes in the partitioning between particle and gas phases.

1. Introduction

Comprehensive study has been made of the formation of aerosol particles in the atmosphere (Bzdek et al., 2011; Kulmala et al., 2004; Vaattovaara et al., 2009), and various ions and molecular clusters have been identified as participating in

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particle formation events (Ehn et al., 2011; Kiendler-Scharr et al., 2009; Manninen et al., 2009). The chemical composition of the growing particles changes during the process (Riipinen et al., 2009). Although information obtained in recent years has clarified our picture of the nucleation process (Kulmala & Kerminen, 2008; Kulmala et al., 2013), the exact organic compounds participating in particle formation have not been identified. Accordingly, there is a need for still faster and more efficient collection systems and for analytical instrumentation capable of providing data on the wide variety of compounds present in nano-sized aerosol particles of very low mass.

The analysis and identification of compounds of extremely small aerosol particles is challenging. Fortunately, recent advances in collection and analysis techniques have increased our knowledge of the different types of compounds present in nanoparticles ($D_p < 50$ nm) and given us a better understanding not only of the chemical composition of aerosols but also of the role of the different functional groups (Ruiz-Jimenez et al., 2011, 2012). Aerosol mass spectrometers have become important tools in aerosol chemistry and in the elucidation of changes in chemical composition of atmospheric aerosols (Hartonen et al., 2011; Pratt & Prather, 2012). One of the shortcomings of aerosol mass spectrometers is that they produce mixed mass spectra of the compounds in aerosol particles, and in ambient measurements it is extremely difficult to determine the role of individual organic compounds. Although MS/MS techniques would be helpful (Kampf et al., 2011; Warnke et al., 2006), they are not yet widely employed. Off-line analysis of extracted filter or impactor samples can be performed by analytical techniques such as GC–MS and LC–MS, which can be applied, alone or in parallel, for the analysis and identification of individual compounds. Chromatographic techniques in combination with mass spectrometry or NMR generally are an excellent choice for obtaining molecular information (Korhammer & Bernreuther, 1996), but usually they cannot be applied for in-situ analysis of aerosol particles. One viable approach to the study of organic compounds in nucleation-mode particles, and the approach adopted here, is to use an aerosol mass spectrometer for in-situ investigation of interesting phenomena and to carry out complementary and supportive analysis in the laboratory on simultaneously collected filter samples.

Recent studies have demonstrated the relevance of nitrogen-containing compounds in particle growth processes (Kulmala & Petäjä, 2011). Moreover, soil emissions are considered to be a source of nitrogen compounds in the atmosphere (Ge et al., 2011a, b; Miyazaki et al., 2012). Nitrogen-containing compounds have also been observed in small clusters (below 2 nm) (Ehn et al., 2010) in APi-TOFMS measurements at boreal forest site. The chemical relations between compounds in the gas phase, small clusters, and ultrafine aerosol particles remain to be studied. We used laser AMS to monitor the changes in chemical composition of 10 nm aerosol particles collected in boreal forest environment in the years 2010 and 2011. Emphasis was put on measurement of nitrogen-containing compounds in 10 nm particles, and particularly on the identification of the frequently detected ions m/z 143 and 185. Re-analysis of 30 nm particles from filter samples collected simultaneously in 2011 showed these ions to be derived from quinoline compounds, which also appeared in the molecular clusters measured by APi-TOFMS.

2. Experimental

Aerosol on-line measurements were carried out at the boreal forest site of the SMEAR II station (Station for Measuring Ecosystem-Atmosphere Relations) in Hyytiälä, Finland (Hari & Kulmala, 2005), between April 28 and October 13, 2010, and from March 14 to May 16, 2011. The instrumentation is briefly described below.

2.1. Laser AMS measurements

The laser aerosol mass spectrometer (laser AMS) (Laitinen et al., 2009) measures the chemical composition of sub-50 nm particles (10 nm during this study) pre-selected with a differential mobility analyzer (DMA). Although the laser AMS provides sample collection efficiency of $> 90\%$ for 10 nm particles, collection times typically varied from 5 to 14 days (see Table SI-1) to allow the instrument collect a sufficient sample amount (approximately 1 ng) for analysis.

Size classification was done with a Vienna-type DMA (Winklmayr et al., 1991) operated with 10 litre per minute (lpm) sheath flow rate and 3 lpm sample flow rate. The size-separated and negatively charged particles are directed to a positively charged collection surface (+2 kV during this study) mounted on a custom-made ball valve. The collected sample is introduced to the high vacuum (10^{-8} Torr) of the mass spectrometer by rotating the sampling valve. The sample material is desorbed from the collection surface with an IR laser (1064 nm wavelength), and the cloud of volatilized molecules is ionized with a UV laser (193 nm wavelength). The ions are guided with ion lens system to an orthogonal compact time-of-flight mass spectrometer (CTOFMS, Tofwerk AG, Switzerland) and detected according to their flight times. The Laser AMS has been described previously (Laitinen et al., 2009) and its applicability for the determination of atmospheric aerosol composition is tested and verified (Laitinen et al., 2010, 2011).

For each aerosol sample, a combined mass spectrum was calculated from 21 laser shots and normalized to total ion count. The combined mass spectrum was mass calibrated using ions originating from the collection surface and characteristic for the instrument (Mn, Fe, Cr, Na, K) (Junninen et al., 2010). The spectra were baseline corrected, where the baseline was estimated from a 0.2 amu wide window between the peaks. Finally, unit mass resolution line spectra were calculated and used for all further analysis. All processing of mass spectral data was done with the tofTools software package (Junninen et al., 2010).