Denuder/Filter Sampling of Organic Acids and Organosulfates at Urban and Boreal Forest Sites: Gas/Particle Distribution and Possible Sampling Artifacts

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Abstract

Carboxylic acids and organosulfates comprise an important fraction of atmospheric secondary organic aerosols formed from both anthropogenic and biogenic precursors. The partitioning of these compounds between the gas and particle phase is still unclear and further research is warranted to better understand the abundance and effect of organic acids and organosulfates on the formation and properties of atmospheric aerosols. This work compares atmospheric aerosols collected at an urban and a boreal forest site using two side-by-side sampling systems; A high volume sampler (HVS) and a low volume (LVS) denuder/filter sampling system allowing for separate collection of gas- and particle-phase organics. All particle filters and denuder samples were collected at H.C. Andersen Boulevard (HCAB), Copenhagen, Denmark in the summer of 2010, and at the remote boreal forest site at Hyytiälä forestry field station in Finland in the

summer of 2012. The chemical composition of gas- and particle-phase secondary organic aerosol was investigated by ultra-high performance liquid chromatography/electrospray ionization quadrupole time-of-flight mass spectrometry (UPLC/ESI-Q-TOFMS), with a focus on carboxylic acids and organosulfates. Results show gas-phase concentrations higher than those observed in the particle phase by a factor of 5-6 in HCAB 2010 and 50-80 in Hyytiälä 2012. Although abundant in the particle phase, no organosulfates were detected in the gas phase at either site. Through a comparison of samples collected by the HVS and the LVS denuder/filter sampling system we evaluate the potential artifacts associated with sampling of atmospheric aerosols. Such comparison shows that particle phase concentrations of semi-volatile organic acids obtained from the filters collected by HVS are more than two times higher than concentrations obtained from filters collected using LVS denuder/filter system. In most cases, higher concentrations of organosulfates are observed in particles collected by HVS compared to samples collected by LVS denuder/filter sampling system. The present study shows that volatile organics may absorb onto filter materials in the HVS (and similar sampling systems without denuder) and furthermore undergo subsequent on-filter oxidation and sulfation resulting in formation of both organic acids and organosulfates.

1. Introduction

Atmospheric aerosols play an important role in processes related to Earth's climate. In the atmosphere, aerosols may result in direct backscattering of solar radiation along with enhanced formation and lifetime of clouds, thus resulting in a net cooling effect on the global climate (WGI, Chapter 8, IPCC, 2013).

The atmospheric oxidation and conversion of both natural and anthropogenic volatile organic compounds (VOC) is considered a major source of atmospheric aerosols. Photochemical

reactions of VOC with OH-radicals in the sunlit atmosphere, photolysis, reaction with O₃ and, during night, with NO₃-radicals all result in the formation of a complex group of semi-volatile (SVOC) and low volatile organic compounds, which partition between the gas and particle phase forming secondary organic aerosol (SOA) (Odum et al., 1996; Hoffmann et al., 1997; Donahue et al., 2006; Kroll and Seinfeld, 2008; Jimenez et al., 2009). Particularly the extremely low-volatile organic compounds (ELVOC, Ehn et al. 2014, Rissanen et al. 2014, Rissanen et al. 2015) recently observed from monoterpenes formed via auto-oxidation reactions after the initial O₃ reactions seem to contribute to the SOA formation (Riccobono et al. 2014).

Depending on location, time, and specific source regions, SOA can be produced from both anthropogenic and biogenic VOCs (AVOC and BVOCs, respectively). Although globally the production of biogenic SOA dominates the production of anthropogenic SOA (Hallquist et al., 2009), there are indications that the anthropogenic emissions can enhance biogenic SOA formation (Carlton et al. 2010, Hoyle et al. 2011, Nguyen et al. 2014).

Organic acids constitute a major ubiquitous group of organic compounds identified in atmospheric SOA (Chebbi and Carlier, 1996; Pavuluri et al., 2010). Due to their low volatility and polar hydrophilic character, the acidic products are of special interest with respect to formation of SOA from both AVOC and BVOC (Warnke et al., 2006; Veres et al., 2008; Paulot et al., 2011; Sommariva et al., 2011; Andrews et al., 2012; Vogel et al., 2013) and their potential high climatic effect through their ability to increase the cloud forming potential of aerosols. Although organic acids can be emitted from primary sources such as biomass burning (Narukawa et al., 1999; Kundu et al., 2010), vehicular exhausts (Kawamura and Kaplan, 1987), cooking (Schauer et al., 2002), and natural marine sources (Kawamura and Sakaguchi, 1999; Mochida et al., 2003; Rinaldi et al., 2011; Fu et al., 2013) the atmospheric photo-oxidation of

various organic precursors, i.e., VOC, are considered the major source of organic acids in SOA (Hatakeyama et al., 1987; Kawamura et al., 1996; Hallquist et al., 2009; Zhang et al., 2010a). Monoterpenes, including α -pinene and β -pinene, are widely recognized as important biogenic precursors of organic acids in SOA (Hoffmann et al., 1997; Yu et al., 1999; Glasius et al., 2000; Zhang et al., 2010a). Atmospheric oxidation of α -pinene and β -pinene by OH-radicals and O_3 has been shown to result in the formation of several so-called first-generation organic acids, including the oxocarboxylic and dicarboxylic acids pinonic, hydrooxy-pinonic acid (OH-pinonic acid), pinic acid, terebic acid, and terpenylic acid (Hoffmann et al., 1998; Glasius et al., 2000; Larsen et al., 2001; Claeys et al., 2009a). The first-generation notation is here applied as reference to the relative fast and early stage formation, hence lower age of these oxidation products.

The composition and properties of atmospheric aerosol continuously evolve as they are aged through a series of chemical transformations in the gas phase or in the condensed particle phase (Jimenez et al., 2009). One example of such transformations is the formation of the highly oxidized 3-methyl-1,2,3-butantricarboxylic acid (MBTCA) from the gas-phase aging of pinonic acid (Szmigielski et al., 2007; Müller et al., 2012). In addition to MBTCA, diaterpenylic acid acetate (DTAA), suggested to form from the OH-initiated oxidation or ozonolysis of α -pinene (Claeys et al., 2009b), has been suggested as a tracer for aged α -pinene SOA (Yasmeen et al., 2012). In the current study, DTAA and MBTCA are thus categorized as second-generation biogenic acids. Pinonic acid, OH-pinonic, terebic acid, terpenylic acid, pinic acid, diaterpenylic acid acetate (DTAA) and 3-methyl-1,2,3-butantricarboxylic acid (MBTCA) have all previously been used as tracers of atmospheric oxidation of BVOCs (Yu et al., 1999; Claeys et al., 2009a;

Hallquist et al., 2009; Zhang et al., 2010a; Yasmeen et al., 2011; Gomez-Gonzalez et al., 2012; Hansen et al., 2014; Nguyen et al., 2014).

Organic acids originating from the atmospheric oxidation of AVOC have been identified in SOA in different remote and urban environments (Zhang et al., 2010a; Hansen et al., 2014; Nguyen et al., 2014). Adipic and pimelic acid from the oxidation cycloheptene and cyclohexene have been recognized as important tracers for anthropogenic pollution, with elevated concentrations observed in urban environments (Hatakeyama et al., 1987; Zhang et al., 2010a). Other important anthropogenic acids include aromatic compounds such as benzoic and phthalic acid. Benzoic acid is a secondary product from photochemical degradation of aromatic hydrocarbons emitted by automobiles (e.g., benzene, toluene) (Suh et al., 2003) and has been measured as primary pollutant in the exhaust of motor vehicles (Kawamura et al., 1985; Rogge et al., 1993). Phthalic acid has been shown to form by photo-degradation of naphthalene and other polycyclic aromatic hydrocarbons (PAHs) (Bunce et al., 1997; Jang and McDow, 1997) and from phthalic esters emitted during open waste burning of plastic material (Simoneit et al., 2005).

Organosulfates (OS) and nitrooxy organosulfates (NOS) constitute an important group of processed (or aged) compounds, since their formation involves the reaction of oxidation products with sulfuric acid, or in the case of NOS, that of NO_x (NO and NO_2) or nitrate radicals (Iinuma et al., 2007; Surratt et al., 2007a; Gomez-Gonzalez et al., 2008; Surratt et al., 2008; Surratt et al., 2010). Different mechanisms have been proposed for the formation of OS and NOS including esterification of hydroxyl groups or keto groups (after gem-diol formation) with sulfuric acid (Liggio and Li, 2006), through reactive uptake of epoxides (Iinuma et al., 2009; Surratt et al., 2010) or through radical-initiated processes in wet aerosols (Minerath and Elrod, 2009; Noziere et al., 2010; Schindelka et al., 2013).

BVOCs, such as isoprene, monoterpenes (α -pinene, β -pinene and limonene), and the oxygenated VOC (OVOC) 2-methyl-3-buten-2-ol (MBO), have been identified as precursors of OS in SOA in ambient air (Iinuma et al., 2007; Surratt et al., 2008; Kristensen and Glasius, 2011; Worton et al., 2011; Zhang et al., 2012b). OS derived from isoprene (Surratt et al., 2007b; Gomez-Gonzalez et al., 2008) and isoprene oxidation products (Gomez-Gonzalez et al., 2008; Zhang et al., 2012a; Lin et al., 2013) are considered the most abundant and ubiquitous in atmospheric aerosol (Surratt et al., 2007a; Froyd et al., 2010; Kristensen and Glasius, 2011; Stone et al., 2012) and have been used as markers of isoprene-derived SOA in field experiments (Froyd et al., 2010; Zhang et al., 2012a; Worton et al., 2013). In addition, OS originating from MBO have recently been identified in ambient aerosols at concentrations comparable to that of the most abundant isoprene-derived OS, thus constituting an important source to biogenic SOA in regions with high MBO emissions (Zhang et al., 2012b).

So far, OS have been observed in both laboratory-generated SOA (Iinuma et al., 2007; Surratt et al., 2007a; Surratt et al., 2008; Iinuma et al., 2009; Surratt et al., 2010) and ambient atmospheric aerosol collected in remote, urban, forested, marine, and arctic locations worldwide (Maria et al., 2003; Romero and Oehme, 2005; Surratt et al., 2007a; Frossard et al., 2011; Kristensen and Glasius, 2011; Mazzoleni et al., 2012; Stone et al., 2012; Hansen et al., 2014; Nguyen et al., 2014). Recently, OS have been observed from aromatic compounds as well (Riva et al., 2015) thus underlining the vast sources of OS in atmospheric aerosols

The distribution of SVOCs between the gas and the particulate phase is arguably one of the most important parameters in describing their atmospheric transport and fate. Atmospheric degradation and deposition strongly depend on the SVOC's presence in the gas or particulate phase, which together combine to limit the long-range atmospheric transport of SVOCs.

135 Additionally, aerosol optical properties, atmospheric lifetime, and behavior as cloud
136 condensation nuclei depend on the carbonaceous material in the particles, thus the partitioning of
137 SVOC (Seinfeld and Pandis, 1998). Quantum mechanical calculations have shown that organic
138 acids in the gas phase can help to surmount the nucleation barrier by forming clusters with
139 sulfuric acid, and thus play an important role in new particle formation (Zhang, 2010). If so,
140 accurate measurements of the presence and abundance of these organic compounds in the gas
141 phase is even more important.

142 Sampling and analysis of atmospheric aerosols that contain SVOC partitioned between the gas
143 and the particle phases has previously been performed (Turpin et al., 2000; Mader et al., 2001;
144 Parshintsev et al., 2011; Bao et al., 2012) and potential artifacts have been discussed. Aerosol
145 filter sampling can be biased by positive (gas-phase condensation, reactions on the filter surface)
146 and/or negative (evaporation during sampling, degradation on the filter surface, losses or
147 degradation during sample preparation and analysis) sampling artifacts (e.g Vogel et al., 2013).
148 Due to risk of gas-phase condensation of semi-volatile compounds onto particle filters it is
149 important to collect atmospheric aerosols in such a way that gaseous compounds are separated
150 from the particle phase without affecting the gas-particle distribution. As the widely-used high
151 volume sampler typically offers no separation between the collection of gas and particle phase,
152 gaseous compounds may be adsorbed to quartz fiber filters, thus resulting in positive bias in the
153 measured particle phase concentration (Hering et al., 1990; Turpin et al., 1994; Mader et al.,
154 2001; Warnke et al., 2006; Parshintsev et al., 2011).

155 In this study we compare early summer aerosol particle and gas samples from an urban site and a
156 boreal forest site. At both locations two instruments were running in parallel: a high volume
157 sampler (HVS) and a low volume filter/denuder sampling system (LVS). The HVS filter data

from the urban site discussed herein represent a subset of filters from the campaign presented by Nguyen et al. (2014). In the current study, additional compounds have been identified and data obtained from the collected filters are presented with greater details compared to the publication by Nguyen et al. (2014). In addition, whereas the focus of Nguyen et al. (2014) is on the anthropogenic influence on the formation of biogenic SOA, the purpose of the work presented here is two-fold: to determine and compare gas and particle concentrations of semi- and low volatile organic compounds at the two sites based on filter and denuder sampling, and to evaluate potential sampling artifacts.

2. Materials and methods

2.1 Field sampling

Aerosol samples were collected during two separate field studies performed at H.C. Andersen's Boulevard (HCAB), Copenhagen, Denmark (June 9-16, 2011, mean day temperature and RH = 16.8 °C, 65% RH, mean night temperature and RH = 15 °C, 81% RH), and at the SMEAR-II (Station for Measuring Forest Ecosystem-Atmosphere Relations, Hari and Kulmala, 2005) forest field station in Hyytiälä, Finland (June 6-19, 2012, mean day temperature and RH = 15.3 °C, 52 % RH, mean night temperature and RH = 11.5 °C, 67 % RH).

The urban curbside station at HCAB is located in central Copenhagen (~1.2 million inhabitants) with considerable traffic influence (~50.000 vehicles per day, Municipality of Copenhagen, www.kk.dk). The SMEAR-II field station is located in a homogeneous Scots pine (*Pinus sylvestris*) stand on a flat terrain at Hyytiälä Forestry Field Station of the University of Helsinki, 220 km northwest from Helsinki, Finland (Fig. 1).

12 hour PM₁ samples were collected daily at 6.00 a.m. and 6.00 p.m. local time at both sites by a Digitel DHA-80 High volume sampler (HVS, Flow rate: ~398 L min⁻¹) onto quartz fiber filters. The quartz fiber substrates (Munktell Filter AB, Falun, Sweden) were prebaked at 600 °C for 6 h prior to sampling. In addition, a low volume denuder/filter sampling system (LVS, Flow rate: ~16 L min⁻¹) was employed for the separate collection of gas- and particle-phase SOA at both sites next to the HVS. The low-volume denuder/filter sampling system consists of a glass tube denuder (length = 30 cm, diameter = 5 cm) coated with Amberlite XAD-4 solid phase adsorbent, and attached to a low volume filter sampler, enabling separation of gas-phase and particle-phase compounds (Mader et al., 2001). XAD-4 was chosen because it is widely used, because of its good adsorption characteristics for volatile organic compounds (Gundel et al., 1995). A schematic of the denuder/filter sampling setup is shown in Figure 1. Air is passed through the glass tube denuder in which gaseous SVOCs diffuse to the XAD-4-coated walls, while particles are transmitted and deposited onto a downstream filter (Advantec 47mm 0.20 micrometer PTFE) in a stainless steel filter holder. In contrast to the quartz fiber filters used in the HVS, PTFE filters used in the LVS minimize the adsorption of gaseous SVOC during sampling (Parshintsev et al., 2011). Once sampling is finished, both filter and glass denuder is extracted and analyzed for particle and gas-phase organic compounds separately.

2.2 Filter adsorption of OVOC

Laboratory tests were performed to investigate reactions of selected OVOC adsorbed onto quartz fiber filters. The following OVOC were used; α -pinene oxide (97%, Sigma-Aldrich), β -pinene oxide (synthesized according to Hill et al. (1974) and MBO ($\geq 98\%$, Sigma-Aldrich). 100 μ L of OVOC was added to an evaporation flask and evaporated at room temperature by N₂. Two 47mm quartz fiber filters (Filter A and Filter B) were placed in separate stainless steel filters

holders downstream of the evaporation flask. Using a small pump, the N₂ stream was split and evaporated OVOC directed through each of the two quartz fiber filters at a flow rate of 10 L min⁻¹. After approximately one hour of sampling, Filter A was removed from the filter holder and extracted in 3 mL of dichloromethane (DCM, ≥99.9%, Chromasolv). The resulting solution was then filtrated by Teflon filters (0.22 µm pore size, Q-Max) and analyzed using a gas chromatograph with a flame ionization detector (GC-FID) to determine the adsorbed amount of OVOC. Filter B was left in the filter holder and used for subsequent atmospheric sampling of total suspended particulates (TSP) performed at Aarhus University campus, Aarhus, Denmark (April 2015). Sampling of TSP onto Filter B was accompanied by parallel sampling onto a clean 47mm quartz fiber filter (placed in a stainless steel filter holder). The sampling was performed for 24 hours at a flow rate of 10 L min⁻¹. After sampling the two filters were extracted and analyzed for SOA as described in the following.

2.3 Sample extraction

Aerosol samples were extracted by ultra-sonication in a 1:1 mixture of acetonitrile and methanol (LC-MS, Chromasolv, 99,9%, Fluka). The resulting extract was filtered by a Teflon filter (0.22 µm pore size, Q-Max) to remove insoluble material and dried completely under N₂. The residue was reconstituted in 250 µL of MilliQ water with 10% acetonitrile and 0.1% acetic acid for analysis. 4 µg of camphoric acid (dissolved in acetonitrile) was added as recovery standard to each filter prior to extraction. A mean recovery of 51 (±10 %) was obtained for all LVS and HVS samples and the concentrations of organic acids were corrected accordingly. Similar recoveries were obtained from extraction of quartz and PTFE filters (51 ±10 % and 51 ±17 %, respectively)

Extractions of the glass denuders in the low volume system were performed by repeated (5 times) washing of the XAD-4 coated glass surface with a 1:1:1 mixture of dichloromethane, hexane, and methanol. The combined extract was reduced in volume under vacuum and reconstituted in a known volume of 50% acetonitrile in water with 0.1% acetic acid. Additional extractions of the denuders showed no remaining organic acids and organosulfates.

2.3 UHPLC-ESI-qTOF-MS analysis and quantification of compounds

All samples were analyzed using an Ultra High Performance Liquid Chromatograph (Dionex UltiMate 3000) coupled to the electrospray ionization source of a Bruker Daltonic quadrupole time-of-flight mass spectrometer (UHPLC-ESI-qTOF-MS) operated in the negative (-) ionization mode. The chromatographic separation was performed on an Acquity UPLC HSS (high strength silica) T3 reversed phase column ($2.1 \times 100\text{mm}$, $1.8\mu\text{m}$ particle size, Waters). The eluent composition was (A) 0.1% acetic acid (LC-MS eluent additive grade, Fluka) in Milli-Q grade water and (B) acetonitrile (LC-MS, Chromasolv, 99,9%, Fluka). The gradient was as follows: constant 0% B for 2 min, increased from 0 to 90% B in 10 min, held constant for 3 min and then returned to 0% B in 1 min. The injection volume was $5\ \mu\text{L}$ and flow rate was $0.3\ \text{mL min}^{-1}$. Column temperature was kept at $40\ ^\circ\text{C}$. The operating conditions of the MS have been described elsewhere (Kristensen and Glasius, 2011).

All organic acids with the exception of OH-pinonic acid and terebic acid were identified and quantified using authentic standards. Seven-point ($0.1 - 5\ \text{mg L}^{-1}$) linear calibration curves ($R^2 > 0.991$) were prepared from the following carboxylic acids: adipic acid, pimelic acid, benzoic acid, phthalic acid, cis-pinic acid, pinonic acid, terpenylic acid, diaterpenylic acid acetate (DTAA), and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA). OH-pinonic acid and terebic acid were quantified using standards of pinonic acid and terpenylic acid, respectively.

OS and NOS were identified by the mass spectrometer from their loss of SO_3^- (m/z 80) or HSO_4^- (m/z 97) and an additional loss of HNO_3^- (m/z 63) in the case of NOS (Surratt et al. 2007). Identified OS were quantified using seven-point ($0.1 - 5 \text{ mg L}^{-1}$) linear calibration curves ($R^2 > 0.993$) of three different OS surrogate standards, depending on the retention time of the individual OS compound (Hansen et al., 2014; Nguyen et al., 2014). The surrogate standards included D-mannose 6-sulfate sodium salt (molecular weight (MW) = 282 g mol^{-1} , $\geq 90\%$ Sigma-Aldrich), an organosulfate from β -pinene (MW = 250 g mol^{-1}), which was synthesized in-house following Iinuma et al. (2009), and sodium octyl sulfate (MW = 232 g mol^{-1} , $\geq 95\%$ Sigma-Aldrich).

3. Results and discussion

Organic acids identified in collected filter and denuder samples are listed in Table 1. Vapor pressure estimates given in Table 1 are calculated using the EVAPORATION model (Compernelle et al., 2011) and three E-AIM models: 1) based on equations by Myrdal and Yalkowsky (1997) with boiling point estimate by the method of Stein and Brown (1994); 2) equations by Moller et al. (2008) using boiling points estimated by the method of Nannoolal et al. (2004), or 3) equations by Nannoolal et al. (2008) using boiling points estimated by the method of Nannoolal et al. (2004). In addition, available experimental determined vapor pressures for the organic acids are given in Table 1 for comparison with estimated values. The OS and NOS identified in this study are listed in Table 2. For sake of comparison, only OS and NOS identified at both HCAB and Hyytiälä are quantified and presented in the following. Organic acids are classified as first-generation biogenic acids, second-generation biogenic acids, and anthropogenic acids, while OS are classified as monoterpene-derived OS, isoprene and MBO-derived OS (isoprene + MBO OS), and monoterpene NOS. Note that although OS MW

154 and OS MW 156 are derived from glycolaldehyde and hydroxyacetone these are here classified as isoprene-derived OS since both glycolaldehyde and hydroxyacetone have been shown to form from isoprene oxidation (Galloway et al. 2011) and both OS show good correlation ($R^2 > 0.7$) with the other isoprene-derived OS.

A total of 11 carboxylic acids and 14 organosulfates were identified from the collected filters at HCAB and Hyytiälä. Aerosol Mass Spectrometer (AMS) measurements by Corrigan et al (2013) estimates the organic fraction of PM_{10} in Hyytiälä during July 2010 to 64%. As data published by Vogel et al. (2013) show organic acids to contribute around 60% to the total organic aerosol mass in Hyytiälä in 2010, the identified acid in the LVS samples presented here is roughly estimated to account for around 2-3% of the total organic acids in aerosols in Hyytiälä. Based on these calculations, the acids identified in this study only represent a small fraction of the total organic acid content present in aerosols in Hyytiälä.

3.1 Gas/particle phase distribution of organic acids and OS

The mean concentrations ($ng\ m^{-3}$) of first-generation biogenic acids, second-generation biogenic acids, anthropogenic acid, isoprene and MBO OS, monoterpene OS, and monoterpene NOS identified in the LVS filters (particle phase) and denuders (gas phase) at HCAB and Hyytiälä are listed in Table 3-4 and illustrated in Figure 2. From the experimentally determined gas and particle concentrations we can calculate the mass-based fraction F_i of compound i in the particle phase (Kroll et al. 2008):

$$F_i = \frac{P_i}{P_i + G_i} \quad (1)$$

Where P_i is the mass concentration of i in the particle phase and G_i is the mass concentration of i in the gas phase. The calculated F -values for all compounds at both HCAB and Hyytiälä are given in Table 3-4.

From Tables 3-4 and Figure 2 it is clear that the highest concentrations of the studied acids are present in the gas phase in the atmosphere at both HCAB and Hyytiälä. At HCAB, the identified anthropogenic acids make up a major fraction of the identified compounds in both gas and particle phase (>86 and 65%, respectively). Gas phase in particular shows significantly higher (> 6 times higher) concentrations of acids from anthropogenic sources compared to biogenic. In accordance with vapor pressures shown in Table 1, benzoic acid dominates the gas phase at HCAB, contributing more than 50 % to the identified gas-phase compounds, followed by adipic acid (~15 %) and phthalic acid (~10 %). Phthalic acid show F -values between 0.19-0.29, adipic acid 0.13-0.15 and benzoic acid 0.09-0.13, consistent with decreasing vapor pressure estimates of the three acids in Table 1. ,

The first-generation biogenic acids at HCAB show significantly higher concentrations (> 6 times higher) in gas phase compared to the particle phase for both day- and night-time samples, with higher gas phase and lower particle phase concentrations in day-time samples compared to night-time samples. The first-generation biogenic acid, pinonic acid, is the most dominant of the biogenic acids identified in the denuder (gas phase) samples with concentrations around 2.73 to 6 ng m^{-3} , while only 0.33-0.37 ng m^{-3} of pinonic acid is found in particle samples corresponding to F -values of 0.06 to 0.12. With the exception of OH-pinonic acid, the particle concentration of the more oxidized and less volatile of the first-generation biogenic acids; terebic acid, pinic acid and terpenylic acid is somewhat higher with concentrations ranging from 0.46-0.84 ng m^{-3} . F -values for terebic acid, terpenylic acid and pinic acid are 0.14-0.15, 0.23-0.35, and 0.33-0.42,

respectively. The most abundant of the biogenic acids identified in the LVS particle samples at HCAB is the highly oxidized and low-volatile MBTCA with concentrations around 3.3 and 5.4 ng m⁻³ in day and night-time samples, respectively. In general, the highest particle phase concentration of both biogenic and anthropogenic acids is associated with the night-time samples at HCAB.

Similar to HCAB, LVS filters and denuders from Hyytiälä show a considerably higher (a factor of 12-20) concentrations of carboxylic acids in the gas phase compared to the particle phase. However, gas-phase concentrations of biogenic acids (257-311 ng m⁻³) are significantly higher than anthropogenic acids (7 – 22 ng m⁻³) in contrast to samples collected at HCAB. Pinonic acid is by far the most abundant in the gas phase with concentrations of 269 and 224 ng m⁻³ in day- and night-time denuder samples, respectively. Although abundant in the gas phase, only around 0.2 ng m⁻³ pinonic acid is found in particle samples in Hyytiälä corresponding to a F-value of around 0.001. The high concentration of pinonic acid in the gas phase (>95%) compared to particle phase at both HCAB and Hyytiälä is not surprising given its relatively high vapor pressure (Table 1) and consistent with the findings of Müller et al. (2012) who through theoretical calculations found the gas-phase fraction of pinonic acid to be 98% (at 283K) in a controlled smog chamber study. This is also in good agreement with results from the San Bernadino National Forest, California, where concentrations of pinonic acid were found to be 202 ng m⁻³ in the gas phase and 0.8 ng m⁻³ in the particle phase (F-value = 0.004, Yu et al., 1999).

In general, all first-generation biogenic acid show high abundance in the gas-phase compared to the particle phase in Hyytiälä. F-values for terebic acid, terpenylic acid and pinic acid in Hyytiälä are 0.18-0.21, 0.13-0.15, and 0.04-0.11, respectively. As observed at HCAB, high gas-phase and lower particle-phase concentrations are associated with day-time samples.

Second-generation biogenic acids constitute a relatively larger fraction (55-75 %) of the analyzed compounds in the particle phase in Hyytiälä compared to HCAB (20-22%). Of the analyzed second-generation biogenic acids, MBTCA is the most abundant with concentration almost ten times higher than DTAA, consistent with findings by Gomez-Gonzalez et al. (2012) from a summer field campaign at Brasschaat, Belgium. The high gas-phase concentrations of pinonic acid in Hyytiälä help explain the larger fraction of second-generation biogenic acids compared to HCAB. In Hyytiälä, increased pinonic acid in the gas-phase may facilitate the formation of MBTCA through the gas-phase oxidation of pinonic acid by OH-radicals, as described by Müller et al. (2010).

For comparison, Yatavelli et al. (2014) reported particle-phase fractions (F-values) for pinonic acid, pinic acid and MBTCA measured by micro-orifice volatilization impactor high resolution time-of-flight chemical ionization mass spectrometer (MOVI-HRToF-CIMS) in aerosol at the NCAR Manitou Forest Observatory field site near Woodland Park, Colorado, USA. Measurements show $F_{\text{pinic acid}}$ between 0.2-0.7 consistent with our findings at HCAB ($F_{\text{pinic acid}} = 0.33-0.42$) but higher than findings from Hyytiälä ($F_{\text{pinic acid}} = 0.04-0.11$). In respect to pinonic acid, Yatavelli et al. (2014) showed higher than modelled F-value between 0.1-0.3. This result is consistent with our findings at HCAB ($F_{\text{pinonic acid}} = 0.06-0.12$) but again significantly higher than the F-values obtained for pinonic acid in Hyytiälä ($F_{\text{pinonic acid}} = 0.001$). Our study show MBTCA to be completely in the particle phase ($F_{\text{MBTCA}} = 1.00$) at both HCAB and Hyytiälä which is in good agreement with model calculation by Yatavelli et al. (2014), who, however, found F-values for MBTCA to be somewhat lower ($F_{\text{MBTCA}} = 0.7-0.95$) based on MOVI-HRToF-CIMS measurements. In general, data obtained from LVS denuder sampling at HCAB presented in the current study show good agreement with measurements reported by Yatavelli et al. (2014).

However, data from Hyytiälä showed lower F-values than reported by Yatavelli et al. (2014). This is especially true for pinonic acid, which show a significantly lower F-value in Hyytiälä compared to HCAB (average F-value of 0.001 versus 0.09, respectively).

The large difference in particle-phase fraction of pinonic acid is partly attributed to difference in particle mass (PM_{10} , Table 1) at HCAB and Hyytiälä (6.84-8.39 and 1.86-2.17 $\mu g m^{-3}$, respectively). However, the PM masses at the two sites do not fully explain the large differences associated with $F_{pinonic}$ at HCAB and Hyytiälä, a difference which seems more pronounced for pinonic acid than any of the other acids identified. The authors speculate, that the large discrepancy between $F_{pinonic\ acid}$ at the two sites could be due to fast and more continuous gas-phase formation of pinonic acid from large biogenic emissions in Hyytiälä. This in combination with a slower than expected partitioning to the particles due to semi-solid or glassy particle phase could be causing a build-up of pinonic acid in the gas phase compared to the particle phase, thus explaining the low $F_{pinonic\ acid}$ in Hyytiälä. On a similar note, slower evaporation from aged semi-solid particles, such as reported by Vaden et al. (2011), would aid to explain the larger than expected $F_{pinonic\ acid}$ at the less biogenic dominated HCAB.

Through a crude calculation the degree of photochemical aging can be estimated by calculating the MBTCA/pinonic acid ratio on a mol/mol basis for both sites (Miyazaki et al., 2012). This approach is possible as the OH-initiated oxidation of pinonic acid has been suggested to be the rate-limiting step in formation of MBTCA (Zhang et al., 2010). To evaluate the degree of photochemical ageing we use the total concentration (gas phase + particle phase) of MBTCA and pinonic acid as obtained from LVS denuder sampling. Applying these concentrations in our calculations result in the following MBTCA/pinonic ratios (mol/mol): Hyytiälä (day) = 0.05, Hyytiälä (night) = 0.04, HCAB (day) = 1.82, HCAB (night) = 0.6. As the MBTCA/pinonic acid

ratio is significantly higher at HCAB, these results indicate that the degree of photochemical ageing of the aerosol is higher at HCAB than in Hyytiälä, and thus may exhibit slower than expected evaporation of semi-volatile constituents (i.e. pinonic acid) as suggested by Vaden et al. (2011).

In addition to the reasons stated above, it is important to note that as the organic fraction of PM_{10} may not be the same at HCAB and Hyytiälä, which could also help explain differences between measured and expected $F_{\text{pinonic acid}}$ values. At present time, no measurement of the organic fraction of PM_{10} at HCAB has been reported.

The general differences in the gas-phase composition regarding anthropogenic and biogenic acids between the two sites are likely due to the different VOC sources as Hyytiälä is predominately categorized as a rural background site with high influence of biogenic emissions (i.e., BVOC) (Hakola et al., 2006; Hakola et al., 2012), while HCAB is located in the city of Copenhagen, thus more influenced by AVOC sources.

Finally, as shown in Tables 3-4 and Figure 2, no OS or second-generation biogenic acids are found in the denuder samples at HCAB and Hyytiälä, although present in the particle phase, which is attributed to the expected low volatility of these highly oxidized and sulfate containing compounds. The lack of the low volatile OS and second-generation biogenic acids in the denuder samples verify the usability of the denuder system, as this indicates that only gas-phase compounds are collected by the coated glass denuder.

Of all the identified compounds, OS derived from isoprene and MBO show high ($12\text{--}17\text{ ng m}^{-3}$) concentrations in particles from both HCAB and Hyytiälä. Although Hyytiälä is mostly dominated by monoterpene emissions (Hakola et al., 2006; Hakola et al., 2012), isoprene and

MBO derived OS concentrations are almost 20 times higher than OS from monoterpenes (Table 4). These results are in accordance with previous findings in Yttri et al. (2011) showing high concentrations of the MW 216 isoprene-derived organosulfate compared to organosulfates from monoterpene in aerosols collected at four Nordic sites (including Hyytiälä), thus highlighting the contributions of isoprene and MBO emissions to the aerosol mass in Nordic boreal forests.

3.2 Gas-particle partitioning

To access the gas-particle partitioning of the individual organic acids quantified and discussed herein we follow the procedure by Yatavelli et al. (2014)

As given by equation (1), experimentally derived F_i -values can be calculated from the acid concentrations found in LVS filter and denuder samples. For comparison, expected or modelled values of F_i can also be obtained via absorption partitioning theory (Pankow 1994):

$$F_i = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (2)$$

Here, C_i^* ($\mu\text{g m}^{-3}$) is the effective saturation mass concentration (Donahue et al, 2006) and C_{OA} (μgm^{-3}) is the total organic aerosol mass concentration. C_i^* is obtained as:

$$C_i^* = \frac{M_i 10^6 \mu\text{g g}^{-1} \zeta_i p_{L,i}^0}{760 \text{ torr atm}^{-1} RT} \quad (3)$$

In Eq. (3), M_i (g mol^{-1}) is the molar mass of compound i , ζ_i is the activity coefficient, which we assume is unity, $p_{L,i}^0$ (torr) is the liquid state (potentially sub-cooled) saturation vapor pressure of i at the temperature T , R ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm K}^{-1} \text{ mol}^{-1}$) is the gas constant, T (K) is the temperature. The two numbers 760 (torr atm^{-1}) and 10^6 ($\mu\text{g g}^{-1}$) are unit conversion factors.

Very few experimentally determined liquid state vapor pressures for SOA species are available (Bilde et al. 2015) and for the species in Table 1 values are only available for adipic acid, pimilic acid and pinic acid.

C_i^* was calculated for all the organic acids discussed herein from the experimentally based vapor pressures as well as from vapor pressures estimated by the EVAPORATION model and E-AIM models (Table 1). Calculations were done at two temperatures for each site (290K and 288K representing day/night at HCAB and 288K/284K at Hyytiälä)

As no organic aerosol mass measurements were available at either site, C_{OA} was estimated based on Differential Mobility Particle Sizer (DMPS) measurements (covering the size ranges 6-700 nm and 3-1000 nm at HCAB and Hyytiälä, respectively) It was assumed that all the mass obtained from these measurements (assuming spherical particles and a density of 1.5) represented organic aerosol.

Figure 3 shows the observed F values as calculated from day- and night-time gas and particle-phase concentrations of organic acids (Table 3-4) as a function of the corresponding C_i^* (binned together in volatility bins as in Donahue et al. (2006)). Increased partitioning from the gas phase to the particle phase during night time is observed at both HCAB and Hyytiälä for all values of C_i^* . Similar observations has been reported by Bao et al. (2012) who noted increased particle phase concentration of diacids during night time sampling of SOA using a denuder-filter pack system. The increased night-time particle-phase fraction of the carboxylic acids observed in this study may due to lower temperatures and increased humidity during night time. Bao et al. (2012) presents the hypothesis that that aerosol water may act as an absorbing medium, thus increasing the gas-particle partitioning.

445 As seen from Figure 4 filter/denuder data from HCAB and Hyytiälä generally show lower
446 particle fraction compared to model predictions for compounds with C^* of 0.1 to $10 \mu\text{g m}^{-3}$. A
447 possible reason for this discrepancy may be that the C_{OA} used in Eq. (2) may overestimate the
448 absorbing organic aerosol mass concentration since it is based on the total mass of the measured
449 aerosols and could include non-absorbing inorganics resulting in lower than expected gas-
450 particle partitioning. This is supported by the AMS measurements by Corrigan et al (2013)
451 estimating the organic fraction of PM_{10} in Hyytiälä during July 2010 to 64%. Furthermore, as the
452 data is limited to a total of 11 carboxylic acids, these do not fully and accurately represent the
453 full picture of organic gas-particle partitioning at the two sites. A valid concern regarding the use
454 of denuders upstream of the collection of particle samples involves the possible removal of
455 SVOC from the collected particle phase (Mader et al., 2001). Evaporation of carboxylic acid
456 from the particles situated on the filter material would result in an underestimation of the particle
457 phase fraction, such as observed in Figure 2. However, as data from the filter/denuder sampling
458 show a higher than modelled particle fraction of more volatile carboxylic acid (C^* of 100 to
459 $10,000 \mu\text{g m}^{-3}$) at both sites, evaporation of semi-volatile may not explain the underestimated
460 particle fractions for compounds with C^* of 0.1 to $10 \mu\text{g m}^{-3}$. The higher than modelled particle
461 fraction observed for more volatile carboxylic acids has also been reported in previous studies
462 (Keene et al., 2004; Liu et al., 2012; Yatavelli et al., 2014) and has been attributed to multiple
463 factors including partitioning of acids to the aqueous phase, slower than expected gas-particle
464 equilibrium (Keene et al., 2004; Liu et al., 2012; Yatavelli et al., 2014) and semi-solid or glassy
465 particle phase with slower than expected mass transfers compared to the presumed sub-cooled
466 liquid state of the particles (Vaden et al., 2010).

As evident from Figure 3, differences in the gas-particle partitioning are observed from the use of different models (EVAPORATION versus E-AIM) for estimating the vapor pressure of the organic acids. These differences are underlined in Figure S2 in supplementary material, showing the gas-particle partitioning of the identified acids with vapor pressure estimates from all four models in Table 1. The vapor pressures predicted by the different models differ in some cases by orders of magnitude. This is in part due to lack of accurate experimental values for model development and validation. The discrepancies in the vapor pressure estimates in Table 1 thus underline the need for accurate vapor pressure estimates as highlighted in Bilde et al. (2015). Of the two sites, gas-particle partitioning obtained from filter/denuder samples show the best agreement with the modelled partitioning at HCAB compared to Hyytiälä (Fig. 3). At HCAB, a general decrease in the particle fraction is observed with increased C^* , as would be expected. In Hyytiälä, however, this trend is less pronounced, with higher gas-particle partitioning of some of the more volatile carboxylic acid compared to acids with lower C^* . One potential explanation is that the assumption of gas-particle equilibrium during the sampling period may not be valid, another explanation is inaccuracy in the prediction of C^* based on the large uncertainty associated with vapor pressure determination as discussed above.

3.3 Comparison of High- and Low-volume filter sampling

Figure 4 shows the concentrations of the analyzed compounds (Table 3 and 4) identified in the simultaneous sampled HVS and LVS filter samples collected at HCAB in 2011 and Hyytiälä in 2012. The data show both day- and night-time samples.

Figure 4A shows differences in the concentrations of the identified acids and OS found in the HVS and LVS filter samples (particle phase) at HCAB. In samples collected by HVS the concentration of anthropogenic acids is higher (a factor of ~1.5) compared to samples collected

by the LVS denuder/filter system. The concentration of OS is very similar between the two sampling systems. However, HVS samples show somewhat increased concentrations of OS from monoterpenes compared to LVS samples. The comparison of HVS and LVS concentrations at HCAB show a significant difference ($p < 0.05$) in both first-generation biogenic acids and anthropogenic acids, while no significant differences ($p > 0.05$) are found in the mean concentrations of second-generation biogenic acids and OS.

Concentrations of the investigated compounds also vary significantly between HVS and LVS samples collected in Hyytiälä (Fig. 4B). The largest difference is observed with respect to pinonic acid, which show a mean particle concentration of 4.4 ng m^{-3} in day-time HVS filter samples and 3.3 ng m^{-3} in night-time HVS samples, corresponding to almost 50 and 25 times higher concentrations than observed in day and night-time LVS filter samples, respectively. Likewise, though less pronounced, terebic, terpenylic acid, pinic acid and OH-pinonic acid are observed at higher concentrations in filter samples from HVS compared to LVS (Table 4). At the Hyytiälä site, the concentrations of first-generation biogenic acids and OS detected in HVS and LVS particle samples are significantly different ($p < 0.05$). In contrast, the low volatile second-generation biogenic acids and anthropogenic acids show no significant differences between the two sampling systems (Fig. 4B)

Figure 5 shows the daily variations of all identified compound classes in HVS and LVS samples (normalized to particle mass derived from DMPS measurements) during the two sampling campaigns. As evident from Figure 5C and D, second-generation biogenic acids show similar variations and abundance in both HVS and LVS samples at HCAB and Hyytiälä, while large differences are seen in the case of first-generation biogenic acids (Fig. 5A and B) at both sites

and anthropogenic acids at HCAB (Fig. 5E). Reasons for this could be: a negative bias on the low volume/filter denuder system or a positive bias in HVS. These will be discussed below.

Possible removal of SVOC from the collected particle phase in the filter/denuder system may result in a negative sampling artifact that could potentially account for the observed differences in particle phase concentration between the two sampling system. As SVOC-free air leaving the denuder is passed through the filters, evaporation of SVOC from the collected particles into the gas phase may occur, thus resulting in lower concentrations of these compounds as observed in this study. However, due to mass transfer limitation in a glassy particle phase, as suggested by Vaden et al. (2011), the evaporation of SVOC from collected particles to SVOC-free air should also be slow, thus limiting the negative sampling artifact associated with evaporation of SVOC from the collected particles to the SVOC-free air in the filter/denuder system. A slow mass transfer from collected particles in the LVS is also evident in the somewhat low temperature effect observed in Figure 6, where increased temperatures only result in a small decrease in the particle concentration of first-generation acids in the LVS. In line with this, Mader et al. (2001) showed that less than 33% of organic carbon mass collected on quartz fiber filters downstream of a XAD-4 coated denuder evaporated during sampling. Furthermore, Mader et al. (2001) concluded that significant evaporation of SVOC from the primary filter is unlikely as no organic carbon was found on gas-adsorbing backup filters situated downstream from the primary filter in a filter/denuder sampling system. Based on these observations, we expect that the significantly lower concentrations found in LVS particle samples are not solely caused by evaporation of SVOC from these filters during sampling.

A more likely explanation of the observed discrepancies is that the HVS samples may be subject to a positive bias most likely from adsorption of gaseous SVOC onto the quartz fiber filters, thus

resulting in increased concentration of the more volatile first-generation biogenic acids in the particle samples. Similar observations have been done by Parshintsev et al. (2011) who showed significant adsorption of SVOCs, such as pinic and pinonic acid, onto quartz fiber filters during the collection of size-selective aerosols in Hyytiälä. The high gas-phase concentrations of first-generation biogenic acids and anthropogenic acids compared to particle phase at HCAB would allow for increased adsorption of these semi-volatile acids onto the quartz fiber filter in the HVS, thus explaining the differences between LVS and HVS filter samples. Likewise, significant gas-phase concentration of first-generation biogenic acids at the Hyytiälä site and thus increased adsorption of these in the HVS would explain the significantly higher concentrations of these acids in the HVS compared to LVS. Since adsorption onto filter material can be described by gas/filter partitioning method (Mader et al., 2001), the concentration of the compounds adsorbed onto quartz fiber filters depends on their gas-phase concentration (Warnke et al., 2006). As low gas-phase concentrations of anthropogenic acids were observed in Hyytiälä, filter adsorption of these acids in the HVS may be insignificant, which explains the similar concentrations of anthropogenic acids in the HVS and LVS (Fig. 5F). Since the low volatile second-generation biogenic acids (MBTCA and DTAA) are not detected in gas-phase samples at either HCAB or Hyytiälä, no positive bias is expected through the sampling by HVS, explaining the similar concentrations and temporal variations of these in the samples collected by the two systems (Fig. 5C and D). These results are in line with the findings of Warnke et al. (2006) showing that more volatile organic compounds (i.e. pinonic acid) produce higher sampling artifacts (up to 50 %) than the less-volatile organics during sampling of SOA.

From Figure 6, a clear temperature dependence is observed in the particle concentration obtained from HVS samples collected in Hyytiälä, where the concentrations of first-generation biogenic

acids show good positive correlation ($R^2 = 0.5$) with temperature. In contrast, concentrations of first-generation biogenic acids in LVS particle samples show a weak negative dependence ($R^2 = 0.13$) on temperature, with slightly higher concentrations observed at lower temperatures. At HCAB the temperature correlation coefficient of the first-generation biogenic acids in HVS and LVS samples were an order of magnitude lower than that observed at Hyytiälä ($R^2 = 0.06$ and 0.03 , respectively). Of the identified acids in HVS samples, pinonic acid showed the best correlation and highest temperature dependence at both HCAB and Hyytiälä. No correlations were found between temperature and second-generation biogenic acids, anthropogenic acids, and OS at either site.

From Figures 6A and 6B differences in concentrations of first-generation biogenic acids in samples collected by HVS and LVS are less pronounced at lower temperatures. At low temperatures, condensation of SVOC increases the fraction in the particle phase compared to the gas phase, thus reducing the positive bias associated with the adsorption of gaseous SVOC in the HVS. In theory, at sufficiently low temperatures, no SVOC should be present in the gas phase, thus resulting in similar concentrations of particle-phase SVOCs in HVS and LVS samples, in line with the trend observed in Figure 6.

3.4 On-filter formation of SOA

OS derived from isoprene and MBO show similar temporal variation and concentration in filter samples collected by LVS and HVS at HCAB (Fig. 5G), while two times higher concentrations of monoterpene OS are observed in HVS samples (Table 3). In Hyytiälä, both isoprene and MBO OS and monoterpene OS show significantly higher concentrations (a factor of five and ten, respectively) in samples collected by the HVS (Table 3). As no OS are found in denuder samples, adsorption of OS from the gas phase onto the HVS filters is highly unlikely. One

possible explanation is the adsorption of gaseous OS precursors, such as alcohols and epoxides of isoprene, monoterpenes, and MBO, and a subsequent sulfation of these on the quartz fibre filter. As the biogenic OVOC concentrations at HCAB are expected to be lower than in Hyytiälä (Kajos et al., 2015), adsorption of these compounds onto the HVS filters at HCAB may be less significant, thus resulting in similar OS concentrations in HVS and LVS samples at this site.

Based on the observations of organic acids and OS in samples collected by the HVS, adsorption of assumed organic precursors to quartz fibre filters was investigated. Figure 7 shows a GC-FID chromatogram of an α -pinene oxide solution (Fig. 7B) and the extract from a quartz fiber filter exposed to α -pinene oxide vapors during sampling (Fig. 7C). The chromatograms show that α -pinene oxide vapor do adsorb onto the quartz filter material during sampling. Similar observations were done with β -pinene oxide and MBO (Fig. 2S) underlining the gas-adsorbing capabilities of quartz fiber filters. UHPLC-ESI-qTOF-MS analysis of aerosols collected onto filters with adsorbed α -pinene oxide and β -pinene oxide show that the adsorbed volatile organics undergo further oxidation and reactions on the quartz filter during sampling. On the α -pinene oxide filter (Fig. 8) significant formation of organic acids are observed after aerosol sampling compared to clean quartz filters. A total extra of 3.9 μg of the acids shown in Figure 8 was observed on filters with 17.3 μg of α -pinene oxide absorbed prior to sampling compared to clean filters. Three of the four observed compounds shown in Figure 8 have previously been identified by Kahnt et al. (2014) as oxidation products from the O_3 -initiated oxidation of α -pinene oxide in ambient and laboratory-generated SOA. This strongly indicates that adsorbed, reactive gas-phase organics, such as α -pinene oxide, may undergo further oxidation on the quartz fiber filters during sampling, thus posing a possible bias in the sampling and quantification of SOA from the HVS sampling. Although α -pinene oxide has been identified as precursor of OS (Surratt et al., 2008;

Iinuma et al., 2009; Eddingsaas et al., 2012) no OS were found in SOA sampled on the α -pinene oxide filter. However, the β -pinene oxide filters show significantly higher concentrations of two organosulfates from β -pinene (OS MW 250 and OS MW 280) compared to clean quartz fiber filters (Fig. 9). These two OS have previously been shown to form from reactive uptake of β -pinene oxide in the presence of acidic sulfate seed particles (Iinuma et al., 2007; Surratt et al., 2008; Iinuma et al., 2009) thus indicating that they result from on-filter sulfation of the adsorbed β -pinene oxide during aerosol sampling. The significantly higher formation of OS from β -pinene oxide compared to α -pinene oxide is consistent with the findings of Iinuma et al. (2009). Iinuma et al. (2009) showed that Lewis or Brønsted acid-catalyzed isomerization involving a tertiary carbocation results in the formation of campholenic aldehyde from α -pinene oxide. This may hinder the formation of OS, which is consistent with the findings in this study where we observe oxidation products of campholenic aldehyde rather than OS from α -pinene oxide.

No acidic oxidation products or OS were identified by UHPLC-ESI-qTOF-MS analysis of the MBO filter after aerosols sampling. This may be due to the lack of epoxide formation from MBO on the filter during sampling. As described by Zhang et al. (2012b) formation of the MW 200 OS (Table 2) proceeds through the formation of an epoxide intermediate from the oxidation of MBO.

4. Implications

Filter sampling and subsequent off-line analysis of atmospheric aerosols are a common and well established procedure in atmospheric research, but since filter sampling offers no separation and no distinction between gas and particle phase, little knowledge is obtained regarding the gas/particle distribution of aerosol constituents. In this study, a low volume filter sampling system with the addition of an XAD-4 coated annular glass denuder show high gas-phase

concentrations of semi-volatile carboxylic acids from both anthropogenic and biogenic sources. The gas-phase concentrations of the semi-volatile carboxylic acids identified in this study are orders of magnitude higher compared to particle phase thus posing an important potential source to new particle formation in the atmosphere. To our knowledge, this study presents the first representation of gas-particle partitioning of a mixture of semi- to low-volatile carboxylic acids based on sampling and off-line quantification of gas- and particle-phase. The partitioning results obtained by the off-line technique used in the present study are comparable to results from online MOVI-HRToF-CIMS in Colorado, USA (Yatavelli et al., 2014). This is especially the case for the more aged aerosol mass at HCAB, supporting the usability of the denuder/filter sampling system for partitioning measurements of the studied carboxylic acids in atmospheric aerosol.

The high gas-phase concentrations of semi-volatile organic acids result in a positive artifact associated with the sampling of filter samples without the use of denuders for gas-phase removal. Adsorption of gas-phase semi-volatile carboxylic acid increases the concentration of these compounds in collected PM samples. Furthermore, the current study shows that OVOCs, such as epoxides of α - and β -pinene, may adsorb to quartz fiber filters during sampling. Subsequent on-filter oxidation and sulfation of adsorbed OVOCs result in the formation of both carboxylic acids and OS, thus posing an until now unrecognized positive bias in the sampling and quantification of these organic tracer classes. The adsorption of OVOC from biogenic sources and the positive bias associated with the on-filter formation of OS is more pronounced in the remote boreal forest site in Hyytiälä compared to the urban HCAB curbside site. This shows, that in areas with high emissions of BVOC, OS could form in significant quantity from the adsorption of organics onto the particle filters, while this is less significant in areas with low direct emissions of BVOC, such as the HCAB site in this study.

5. Conclusions

Investigation of the gas- and particle-phase distribution of organic acids and OS at an urban and boreal forest site showed relatively high concentrations of organic acids in the gas phase at the two sites. At the urban HCAB field site, anthropogenic acids contributed a major fraction of the identified compounds in both gas and particle phase. In contrast, the boreal forest site at Hyytiälä showed only modest concentrations of anthropogenic acids, while biogenic acids dominated both gas and particle phase. Neither OS nor second-generation biogenic acids were identified in the gas phase at either site, attributed to the low volatility of these species. The absence of these compounds in the denuder samples furthermore support that only gas-phase compounds are collected by the XAD-4 coated glass denuder, thus allowing for effective separation and collection of the gas and particle phase.

Comparison of the HVS and LVS filter samples showed significantly higher concentrations of organic acids in filter samples collected by the HVS indicating a positive bias through the adsorption of semi-volatile compounds from the gas phase. In contrast, low-volatile compounds such as the second-generation biogenic acids only present in the particle phase, showed comparable concentrations and temporal variations in both HVS and LVS filter samples. OS showed significantly higher concentrations in HVS samples compared to LVS samples collected in Hyytiälä. The higher OS concentration in HVS samples is attributed to adsorption of SVOC, such as epoxides of β -pinene onto the quartz fiber filters followed by sulfation during sampling of atmospheric aerosols, thus representing a positive bias in the collection of OS on quartz fiber filter in areas with high loading of reactive OVOC. The collection SOA on quartz fiber filters without the use of denuder thus represent both gas-and particle-phase contributions, and should not be regarded as solely representative of particle-phase SOA.

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Table 1. Overview of the organic acids identified in this study at both HCAB and Hyttiälä along with molecular structure, suggested precursors and estimated vapor pressure at 298K calculated using: ^aEVAPORATION model (Compennolle et al., 2011), ^bE-AIM (Moller et al., 2008), ^cE-AIM (Nannoolal et al., 2008), ^dE-AIM (Myrdal and Yalkowsky, 1997). ^e Experimental data from Bilde et al., (2015)

Tracer Class	Name	Molecular Structure	Suggested Precursor	$P_{L,i}^0$ (Pa) at 298 K
Anthropogenic acids	Benzoic Acid		Aromatic hydrocarbons	1.08 ^a 1.76 ^b 4.25x10 ^{-1c} 8.31x10 ^{-1d}
	Adipic Acid		Cyclohexene/Heptene	3.34x10 ^{-4a} 1.21x10 ^{-3b} 3.58x10 ^{-3c} 2.81x10 ^{-2d}
	Pimelic Acid		Fatty acid/Heptene	1.8(±1.0)x10 ^{-4e} 1.09x10 ^{-4a} 3.01x10 ^{-3b} 1.01x10 ^{-3c} 1.26x10 ^{-2d}
	Phthalic Acid		Aromatic hydrocarbons	1.0(±0.5)x10 ^{-4e} 2.25x10 ^{-5a} 4.79x10 ^{-7b} 6.01x10 ^{-5c} 4.68x10 ^{-3d}
	Pinonic Acid		α/β- pinene	1.50x10 ^{-2a} 9.46x10 ^{-3b} 5.97x10 ^{-2c} 1.71x10 ^{-1d}
First-generation biogenic acids	Terebic acid		α-pinene	1.42x10 ^{-1a} 7.54x10 ^{-4b} 1.12x10 ^{-2c} 5.87x10 ^{-2d}
	Terpenylic Acid		α-pinene	4.66x10 ^{-2a} 1.93x10 ^{-4b} 3.71x10 ^{-3c} 2.66x10 ^{-2d}
	Pinic Acid		α/β-pinene	4.62x10 ^{-5a} 1.93x10 ^{-4b} 6.87x10 ^{-4c} 1.03x10 ^{-2d}
	Hydroxy-pinonic acid (OH-pinonic acid)		α-pinene	4.4(±2.2)x10 ^{-5e} 7.47x10 ^{-5a} 1.20x10 ^{-6b} 1.41x10 ^{-4c} 6.53x10 ^{-3d}
	Diaterpenylic acid acetate (DTAA)		α-pinene	1.01x10 ^{-6a} 9.97x10 ^{-7b} 1.22x10 ^{-5c} 1.34x10 ^{-3d}
Second-generation biogenic acids	3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)		α/β-pinene	7.28x10 ^{-9a} 5.24x10 ^{-8b} 8.92x10 ^{-8c} 3.03x10 ^{-4d}

Table 2. Overview of the organosulfate (OS) and nitrooxy organosulfates (NOS) identified in this study along with molecular formula, molecular structure and suggested precursors. ^aSurratt et al. (2007a) ^bSurratt et al. (2008) ^cSurratt et al. (2010) ^dGomez-Gonzalez et al. (2008) ^eIinuma et al. (2007) ^fZhang et al. (2012b) ^gGomez-Gonzalez et al. (2008)

Tracer Class	ID	Molecular formula	Possible Structure	Suggested Precursor
Isoprene & MBO OS	OS MW 154	C ₃ H ₆ O ₃ S		Glycolaldehyde ^{a,b}
	OS MW 156	C ₂ H ₄ O ₆ S		Hydroxyacetone ^{a,b}
	OS MW 170	C ₃ H ₆ O ₆ S		Isoprene ^b
	OS MW 200	C ₅ H ₁₂ O ₆ S		MBO ^f
		C ₄ H ₈ O ₇ S		Isoprene ^g
	OS MW 210	C ₅ H ₈ O ₇ S	Unknown	Isoprene
	OS MW 212	C ₅ H ₈ O ₇ S	Unknown	Isoprene ^b
	OS MW 214	C ₅ H ₁₀ O ₇ S		Isoprene ^{b,c}
	OS MW 216	C ₅ H ₁₂ O ₇ S		Isoprene ^{a,c,d}
Monoterpene OS	OS MW250	C ₁₀ H ₁₈ O ₅ S		α/β -pinene ^{a,e}
	OS MW 252	C ₉ H ₁₆ O ₆ S		Limonene ^b
	OS MW 280	C ₁₀ H ₁₆ O ₇ S		α/β -pinene ^a
Monoterpene NOS	NOS MW 295	C ₁₀ H ₁₇ NO ₇ S		α/β -pinene ^{a,b}
	NOS MW 297	C ₁₀ H ₁₅ NO ₈ S		Limonene ^b
	NOS MW 374	C ₁₀ H ₁₈ N ₂ O ₁₁ S		Limonene ^{b,c}

Table 3. Day- and night-time mean concentrations (ng m⁻³) of 1st generation biogenic acids, 2nd generation biogenic acids, anthropogenic acids, and organosulfates (OS) and nitrooxy organosulfates (NOS) from isoprene, MBO and monoterpenes identified in denuder, LVS and HVS filter samples collected at HCAB 2011 (n = 13) (Nguyen et al., 2014). Particle fractions (Fp) of individual compounds are calculated from LVS denuder and filter samples.

HCAB 2011	-Gas phase- LVS Denuder (ng m ⁻³)		-Particle phase- LVS Filter (ng m ⁻³)		Particle fraction, Fp		-Particle phase- HVS Filter (ng m ⁻³)		Gaseous adsorption and artifact fraction for HVS	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Terebic acid	3.19	3.33	0.51 (±0.20)	0.59 (±0.21)	0.14	0.15	0.79 (±0.13)	0.97 (±0.37)	0.35	0.37
Terpenylic acid	1.51	1.28	0.46 (±0.10)	0.70 (±0.23)	0.23	0.35	1.72 (±0.58)	2.48 (±0.93)	0.73	0.72
Pinonic acid	5.60	2.73	0.33 (±0.12)	0.37 (±0.14)	0.06	0.12	1.63 (±0.56)	2.06 (±0.79)	0.80	0.82
OH-pinonic acid	1.13	0.73	0.03 (±0.02)	0.07 (±0.03)	0.03	0.09	0.09 (±0.03)	0.14 (±0.07)	0.67	0.50
Pinic acid	1.35	1.15	0.67 (±0.17)	0.84 (±0.22)	0.33	0.42	0.45 (±0.06)	0.70 (±0.16)	-0.49	-0.20
<i>Σ1st gen. Bio acids</i>	12.78	9.22	2.00 (±0.25)	2.57 (±0.89)	0.14	0.22	4.68 (±1.22)	6.35 (±2.03)	0.57	0.52
DTAA	n.d	n.d	0.13 (±0.06)	0.27 (±0.26)	1.00	1.00	0.20 (±0.07)	0.31 (±0.24)	0.35	0.13
MBTCA	n.d	n.d	3.20 (±1.40)	5.09 (±5.79)	1.00	1.00	3.95 (±2.00)	5.56 (±4.26)	0.19	0.08
<i>Σ2nd gen. Bio acids</i>	n.d	n.d	3.33 (±1.50)	5.36 (±5.00)	1.00	1.00	4.15 (±2.06)	5.87 (±4.49)	0.20	0.08
Adipic acid	15.02	10.28	2.18 (±1.17)	1.80 (±0.64)	0.13	0.15	4.03 (±1.14)	4.89 (±1.15)	0.46	0.63
Pimelic acid	3.45	3.54	0.45 (±0.06)	0.60 (±0.32)	0.12	0.14	0.90 (±0.23)	1.28 (±0.33)	0.50	0.53
Benzoic acid	51.49	41.72	4.82 (±1.94)	6.42 (±5.46)	0.09	0.13	7.48 (±1.37)	6.79 (±2.63)	0.36	0.05
Phthalic acid	12.37	9.98	2.82 (±0.48)	4.05 (±2.80)	0.19	0.29	3.51 (±1.14)	2.21 (±0.64)	0.20	-0.83
<i>Σanthropogenic acid</i>	82.33	65.52	10.27 (±2.37)	11.07 (±4.8)	0.11	0.14	15.91 (±2.42)	15.17 (±3.98)	0.35	-1.14
Σacids	95.11	74.75	15.60 (±2.29)	19.00 (±7.97)	0.14	0.20	24.47 (±3.05)	27.00 (±6.86)	0.36	0.30
OS 154	n.d	n.d	1.64 (±0.47)	2.13 (±1.00)	1.00	1.00	0.70 (±0.58)	1.24 (±0.62)	-1.34	-0.72
OS 156	n.d	n.d	2.28 (±0.88)	2.25 (±0.74)	1.00	1.00	2.40 (±1.47)	2.61 (±0.87)	0.05	0.14
OS 170	n.d	n.d	2.65 (±0.75)	2.55 (±0.86)	1.00	1.00	1.17 (±0.52)	1.52 (±0.62)	-1.26	-0.68
OS 200	n.d	n.d	2.27 (±0.82)	3.29 (±1.47)	1.00	1.00	2.36 (±1.26)	3.78 (±1.78)	0.04	0.13
OS 210	n.d	n.d	0.25 (±0.12)	0.60 (±0.36)	1.00	1.00	0.14 (±0.04)	1.00 (±1.18)	-0.79	0.40
OS 212	n.d	n.d	1.49 (±0.75)	2.14 (±1.14)	1.00	1.00	1.34 (±0.95)	1.84 (±1.00)	0.11	-0.16
OS 214	n.d	n.d	1.10 (±0.56)	1.63 (±0.84)	1.00	1.00	1.05 (±0.76)	1.55 (±0.73)	-0.05	-0.05
OS 216	n.d	n.d	2.34 (±1.03)	2.30 (±0.90)	1.00	1.00	1.12 (±0.79)	1.73 (±0.43)	-1.09	-0.33
<i>Σisoprene + MBO OS</i>	n.d	n.d	14.01 (±4.05)	16.90 (±5.49)	1.00	1.00	10.29 (±5.86)	15.26 (±5.04)	-0.36	-0.11
OS 250	n.d	n.d	0.15 (±0.07)	0.24 (±0.12)	1.00	1.00	0.95 (±0.44)	1.46 (±0.63)	0.84	0.84
OS 252	n.d	n.d	0.06 (±0.02)	0.14 (±0.08)	1.00	1.00	0.07 (±0.08)	0.56 (±0.16)	0.14	0.75
OS 280	n.d	n.d	0.37 (±0.44)	0.64 (±0.57)	1.00	1.00	0.06 (±0.04)	0.24 (±0.17)	-5.17	-1.67
<i>Σmonoterpene OS</i>	n.d	n.d	0.58 (±0.43)	1.01 (±0.64)	1.00	1.00	1.08 (±0.53)	2.25 (±0.89)	0.46	0.55
NOS 295	n.d	n.d	0.03 (±0.01)	0.04 (±0.02)	1.00	1.00	0.13 (±0.03)	0.41 (±0.26)	0.77	0.90
NOS 297	n.d	n.d	b.d	b.d	b.d	b.d	0.01 (±0.01)	0.02 (±0.01)	1.00	1.00
NOS 374	n.d	n.d	b.d	b.d	b.d	b.d	b.d	0.003 (±0.002)	1.00	1.00
<i>Σmonoterpene NOS</i>	n.d	n.d	0.03 (±0.01)	0.04 (±0.02)	1.00	1.00	0.14 (±0.04)	0.44 (±0.27)	0.79	0.91
ΣOS	n.d	n.d	14.63 (±4.02)	17.95 (±5.59)	1.00	1.00	11.50 (±6.34)	17.95 (±5.69)	-0.27	0.00
PM₁ (ugm⁻³)			6.84 (±1.21)	8.39 (±2.51)			6.84 (±1.21)	8.39 (±2.51)		

1106 Table 4. Day- and night-time mean concentrations (ng m^{-3}) of 1st generation biogenic acids, 2nd generation biogenic acids, anthropogenic acids,
1107 and organosulfates (OS) and nitrooxy organosulfates (NOS) from isoprene, MBO and monoterpenes identified in denuder, LVS and HVS filter
1108 samples collected at Hyytiälä 2012 (n = 22).

Hyytiälä 2012	-Gas phase- Low vol Denuder (ng m^{-3})		-Particle phase- Low vol Filter (ng m^{-3})		Particle fraction, Fp		-Particle phase- Hi Vol Filter (ng m^{-3})		Gaseous adsorption and artifact fraction for HVS	
	Day	Night	Day	Night	Day	Night	Day	Night	Day	Night
Terebic acid	8.1	6.16	1.73 (± 1.69)	1.68 (± 1.68)	0.18	0.21	4.31 (± 1.26)	3.54 (± 0.98)	0.60	0.53
Terpenylic acid	6.29	5.61	0.94 (± 0.64)	1.08 (± 0.64)	0.13	0.15	5.17 (± 2.29)	3.67 (± 1.28)	0.82	0.71
Pinonic acid	269.18	224.06	0.17 (± 0.03)	0.18 (± 0.05)	0.001	0.001	8.81 (± 5.67)	4.72 (± 1.69)	0.98	0.96
OH-pinonic acid	5.4	3.92	0.94 (± 1.09)	0.70 (± 0.83)	0.15	0.15	1.92 (± 0.86)	1.19 (± 0.49)	0.51	0.41
Pinic acid	22.22	17.28	0.81 (± 0.54)	2.16 (± 1.25)	0.04	0.11	4.41 (± 2.27)	3.29 (± 1.69)	0.82	0.34
$\Sigma 1^{\text{st}} \text{ gen. Bio acids}$	311.19	257.03	4.59 (± 2.95)	5.68 (± 3.59)	0.02	0.02	24.62 (± 9.57)	16.40 (± 6.54)	0.81	0.65
DTAA	n.d	n.d	1.07 (± 0.29)	1.18 (± 0.48)	1.00	1.00	1.56 (± 0.45)	1.50 (± 0.50)	0.31	0.21
MBTCA	n.d	n.d	10.77 (± 3.13)	11.13 (± 3.42)	1.00	1.00	9.65 (± 1.94)	8.88 (± 2.46)	-0.12	-0.25
$\Sigma 2^{\text{nd}} \text{ gen. Bio acids}$	n.d	n.d	11.83 (± 3.41)	12.30 (± 3.88)	1.00	1.00	11.22 (± 2.36)	10.38 (± 2.95)	-0.05	-0.18
Adipic acid	4.19	2.22	1.26 (± 0.52)	1.21 (± 0.65)	0.23	0.35	1.05 (± 0.66)	0.87 (± 0.60)	-0.20	-0.39
Pimelic acid	1.26	0.89	0.34 (± 0.17)	0.38 (± 0.24)	0.21	0.30	0.09 (± 0.04)	0.05 (± 0.01)	-2.78	-6.60
Benzoic acid	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d	n.d
Phthalic acid	16.77	4.14	2.08 (± 0.72)	2.50 (± 0.86)	0.11	0.34	2.66 (± 0.81)	2.34 (± 0.93)	0.22	-0.10
$\Sigma \text{anthropogenic acid}$	22.22	7.25	3.68 (± 1.97)	4.09 (± 1.57)	0.14	0.36	3.80 (± 1.32)	3.26 (± 1.20)	0.03	-0.25
Σacids	333.41	264.28	15.85 (± 9.25)	22.06 (± 6.54)	0.05	0.08	39.62 (± 12.33)	29.81 (± 9.89)	0.60	0.26
OS 154	n.d	n.d	1.99 (± 0.68)	2.26 (± 0.94)	1.00	1.00	8.45 (± 2.76)	7.43 (± 1.99)	0.76	0.70
OS 156	n.d	n.d	2.28 (± 0.79)	2.53 (± 1.39)	1.00	1.00	8.44 (± 2.89)	8.05 (± 2.37)	0.73	0.69
OS 170	n.d	n.d	0.37 (± 0.16)	0.39 (± 0.16)	1.00	1.00	3.34 (± 0.93)	2.91 (± 0.70)	0.89	0.87
OS 200	n.d	n.d	0.72 (± 0.30)	0.83 (± 0.57)	1.00	1.00	8.03 (± 3.21)	8.23 (± 2.70)	0.91	0.90
OS 210	n.d	n.d	0.13 (± 0.06)	0.20 (± 0.08)	1.00	1.00	2.48 (± 1.05)	2.28 (± 0.61)	0.95	0.91
OS 212	n.d	n.d	1.53 (± 0.47)	1.91 (± 0.99)	1.00	1.00	8.98 (± 3.59)	8.10 (± 3.62)	0.83	0.76
OS 214	n.d	n.d	0.72 (± 0.36)	0.94 (± 0.46)	1.00	1.00	5.68 (± 1.77)	5.43 (± 1.26)	0.87	0.83
OS 216	n.d	n.d	4.17 (± 2.59)	5.33 (± 2.61)	1.00	1.00	14.33 (± 10.75)	15.67 (± 10.09)	0.71	0.66
$\Sigma \text{isoprene} + \text{MBO OS}$	n.d	n.d	11.91 (± 4.33)	14.39 (± 5.88)	1.00	1.00	59.73 (± 20.88)	58.09 (± 17.61)	0.80	0.75
OS 250	n.d	n.d	0.41 (± 0.21)	0.44 (± 0.27)	1.00	1.00	2.62 (± 0.72)	2.36 (± 0.87)	0.84	0.81
OS 252	n.d	n.d	0.04 (± 0.03)	0.09 (± 0.10)	1.00	1.00	1.29 (± 1.22)	1.05 (± 0.58)	0.97	0.91
OS 280	n.d	n.d	0.15 (± 0.09)	0.18 (± 0.11)	1.00	1.00	3.10 (± 2.58)	2.49 (± 1.31)	0.95	0.93
$\Sigma \text{monoterpene OS}$	n.d	n.d	0.42 (± 0.37)	0.71 (± 0.43)	1.00	1.00	6.81 (± 4.32)	5.88 (± 2.19)	0.94	0.88
NOS 295	n.d	n.d	0.12 (± 0.20)	0.07 (± 0.13)	1.00	1.00	0.09 (± 0.08)	0.04 (± 0.04)	0.87	-0.75
NOS 374	n.d	n.d	0.002 (± 0.006)	0.001 (± 0.00)	1.00	1.00	0.005 (± 0.003)	0.003 (± 0.002)	0.60	0.67
NOS 297	n.d	n.d	b.d	b.d	1.00	1.00	0.006 (± 0.005)	0.003 (± 0.004)	1.00	1.00
$\Sigma \text{monoterpene NOS}$	n.d	n.d	0.12 (± 0.18)	0.07 (± 0.13)	1.00	1.00	0.11 (± 0.08)	0.05 (± 0.05)	-0.09	0.86
ΣOS	n.d	n.d	12.69 (± 4.42)	15.17 (± 6.19)	1.00	1.00	66.63 (± 23.40)	64.02 (± 19.18)	0.81	0.76
PM_{10} ($\mu\text{g m}^{-3}$)			1.86 (± 0.63)	2.17 (± 0.62)			1.86 (± 0.63)	2.17 (± 0.62)

Figure 1. **A)** Map of Northern Europe including location of the two sampling sites Copenhagen (Denmark) and Hyytiälä (Finland). **B)** Schematic of denuder/filter sampling system used for collection of gas- and particle-phase SOA.

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Figure 2. Concentration (ng m⁻³) of first-generation biogenic acids (1st gen. biogenic acids, Light Green), second-generation biogenic acids (2nd gen. biogenic acids, Dark Green lined), anthropogenic acids (Red lined), isoprene and MBO OS (Light blue), monoterpene OS, and monoterpene nitrooxy OS (Monoterpene NOS) identified in the LVS filters (particle phase) and denuders (gas phase) collected at **A**) HCAB, Copenhagen, Denmark and **B**) Hyytiälä, Finland.

Figure 3. Gas-particle partitioning (F = fraction in particle phase) of identified organic acids (Table 1) in samples collected by denuder/filter system at HCAB (A, C) and Hyytiälä (B, D) represented by “the volatility basis set”. Saturation concentrations of each acid are calculated by EVAPORATION (Compernelle et al., 2011) (A, B) and E-AIM (Nannoolal et al., 2008) (C, D). Modeled F -values (F model) calculated from Eq. (2) are given for day- (dotted line) and night-time (solid line) conditions. Details on the distribution of acids in each of the nine volatility bins are given in Table 1S and 2S in supplementary material.

Figure 4. Concentration (ng m⁻³) of first-generation biogenic acids (1st gen. biogenic acids, green), second-generation biogenic acids (2nd gen. biogenic acids, dark green with lines), anthropogenic acids (red, lined), isoprene and MBO OS (light blue), monoterpene OS (dark blue), and monoterpene nitrooxy OS (Monoterpene NOS, black) identified in the day- and night-time filters collected by HVS and LVS denuder/filter system at **A)** HCAB, Copenhagen, Denmark and **B)** Hyytiälä, Finland.

Figure 5. Temporal variations of first-generation biogenic acids (1st gen. bio acids), second-generation biogenic acids (2nd gen. bio acids), anthropogenic acid, OS and NOS identified in the day- and night-time (grey highlight) filter samples collected by HVS (♦) and LVS denuder/filter system (■) at HCAB, Copenhagen, Denmark and Hyytiälä, Finland.

Figure 6. Correlation plots of the concentration (ng m⁻³) of first-generation biogenic acids and temperature (°C) for filter samples collected by HVS (♦) and LVS denuder/filter system (■) at A) HCAB, Copenhagen, Denmark and B) Hyytiälä, Finland.

Figure 7. GC-FID Chromatograms of **A)** clean quartz fiber filter extracted in DCM, **B)** α -pinene oxide standard dissolved in DCM, **C)** Quartz fiber filter with adsorbed α -pinene oxide extracted in DCM.

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Figure 8. Extracted ion chromatograms (EIC m/z) of compounds identified from LC/MS analysis of aerosols collected on clean quartz fiber filter (blue) and filter containing α -pinene oxide adsorbed prior to aerosol sampling (red).

Figure 9. Extracted ion chromatograms (EIC) of compounds identified from LC/MS analysis of aerosols collected on clean quartz fiber filter (blue) and filter containing β -pinene oxide adsorbed prior to aerosol sampling (red).