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Denuder/filter sampling of organic acids and organosulfates at urban and boreal forest sites: Gas/particle distribution and possible sampling artifacts

Kasper Kristensen [a, *], Merete Bilde [a], Pasi P. Aalto [b], Tuukka Petäjä [b], Marianne Glasius [a]

[a] *Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Aarhus, Denmark*
[b] *Department of Physics, FI-00014 University of Helsinki, Finland*

HIGHLIGHTS

- This work compares atmospheric aerosols collected at an urban and a boreal forest site.
- Gas/particle partitioning of carboxylic acids and organosulfates is investigated.
- Potential artifacts associated with sampling of atmospheric aerosols are evaluated.
- Different gas/particle partitioning of carboxylic acids observed at urban and boreal forest site.
- Filter adsorption and conversion of semi-volatiles result in biased particle concentrations.

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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.

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* Corresponding author.
E-mail address: kasper.kristensen@chem.au.dk (K. Kristensen).

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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 O_3 and, during night, with NO_3-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, 2015) recently observed from monoterpenes formed via auto-oxidation reactions after the initial O_3 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., 2013a,b) 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., 2010).

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., 2010). 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, hydroxy-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., 2009). 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, 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., 2009; Hallquist et al., 2009; Zhang et al., 2010; 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., 2010; 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., 2010). 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 photodegradation 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, 2008, 2010; Gomez-Gonzalez et al., 2008). 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, 2009; Surratt et al., 2007a, 2008, 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.,