



Potential of needle trap microextraction–portable gas chromatography–mass spectrometry for measurement of atmospheric volatile compounds

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Abstract. Volatile organic compounds (VOCs) play a key role in atmospheric chemistry and physics. They participate in photochemical reactions in the atmosphere, which have direct implications on climate through, e.g. aerosol particle formation. Forests are important sources of VOCs, and the limited resources and infrastructures often found in many remote environments call for the development of portable devices. In this research, the potential of needle trap microextraction and portable gas chromatography–mass spectrometry for the study of VOCs at forest site was evaluated. Measurements were performed in summer and autumn 2014 at the Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II) in Hyytiälä, Finland. During the first part of the campaign (summer) the applicability of the developed method was tested for the determination of monoterpenes, pinonaldehyde, aldehydes, amines and anthropogenic compounds. The temporal variation of aerosol precursors was determined, and evaluated against temperature and aerosol number concentration data. The most abundant monoterpenes, pinonaldehyde and aldehydes were successfully measured, their relative amounts being lower during days when particle number concentration was higher. Ethylbenzene, *p*- and *m*-xylene were also found when wind direction was from cities with substantial anthropogenic activity. An accumulation of VOCs in the snow cover was observed in the autumn campaign. Results demonstrated the successful applicability of needle trap microextraction and portable gas chromatography–mass

spectrometry for the rapid in situ determination of organic gaseous compounds in the atmosphere.

1 Introduction

Earth's atmosphere contains at trace levels a large variety of different volatile compounds that are produced from biogenic and anthropogenic sources. These trace gases can influence air quality and climate through the greenhouse effect (e.g. CO₂ and CH₄) and participation in atmospheric aerosol nucleation and growth (Kulmala, 2003).

Aerosols have a significant impact on climate, both directly, by scattering and absorbing radiation, and indirectly by acting as a cloud condensation nuclei (CCN) and ice nuclei (IN) that naturally affect cloud properties (Zelenyuk et al., 2010). Particles are classified as primary aerosols, when they are directly emitted into the atmosphere, and secondary organic aerosols (SOA), when they are formed from gaseous biogenic or anthropogenic precursors in the atmosphere (Reinhardt et al., 2007). Secondary aerosol formation is recognized as the main source of aerosol particles in the global atmosphere, and organic vapours play a key role on their nucleation and growth mechanisms (Kulmala et al., 2013).

Many organic compounds found in the atmosphere, of both anthropogenic and biogenic origin, have been found to produce SOA (e.g. Seinfeld and Pankow, 2003). The role of volatile organic compounds (VOCs) as a source of natural aerosols has been thoroughly studied in the background regions of the Northern Hemisphere. Coniferous forests produce large amounts of volatile vapours, especially terpenes (Bäck et al., 2012). In temperate and boreal regions, monoterpenes dominate all biogenic VOC (BVOC) emissions, α -pinene and Δ^3 -carene being the most emitted species (Rinne et al., 2009; Yassaa et al., 2012). Monoterpene emissions are mainly dependent on temperature, although the influence of solar radiation and reaction to stress including physical damage, herbivorous attack, drought and heat have also been reported (Nölscher et al., 2012). Monoterpenes are oxidized in the atmosphere, and the produced oxygenated VOCs contribute to new particle formation and growth (e.g. Hao et al., 2009; Kourtchev et al., 2008; Laaksonen et al., 2008). Carbonyl compounds, such as aldehydes, are also important to atmospheric chemistry due to their atmospheric photolysis, reaction with hydroxyl and nitrate radicals, and their contribution to new particle formation (Atkinson, 2000; Jang and Kamens, 2001). Aldehydes can be directly emitted to the atmosphere from incomplete combustion of biomass and fossil fuels, by vegetation, when exposed to stress conditions such as ozone exposure or insect and pathogen attacks, and formed in the atmosphere as a result of photochemical oxidation of reactive compounds (Altemose et al., 2015; Wildt et al., 2003). Primary emissions of saturated C₆–C₁₀ aldehydes, such as hexanal, heptanal, octanal, nonanal and decanal, were found from several particular plant species (Wildt et al., 2003). The photo-oxidation products of benzene, toluene, ethylbenzene and *m*-, *p*- and *o*-xylene (BTEX) are compounds that are also recognized as important precursors of SOA (Li et al., 2014). BTEX sources are very diverse but vehicular exhausts and industrial emissions are considered the major ambient sources (e.g. Scheff and Wadden, 1993). An enhanced stabilization and nucleation rate by atmospheric basic compounds has been confirmed at given sulfuric acid and water concentrations (e.g. Chen et al., 2012; Kurtén et al., 2008; Yu et al., 2012). For example, alkylamines were found to participate in the formation and growth of sub-3-nm particles (Yu et al., 2012). These compounds are emitted both from anthropogenic and biogenic sources, but due to their limited lifetimes, they are not transported long distances in the atmosphere. In forest atmosphere, amine concentrations seem to be linked with vegetation, soil activity, and litterfall (Kieloaho et al., 2013).

Sampling of VOCs is mainly performed by using cartridges filled with an adsorbent material consisting usually of Tenax TA/Carbopack-B that are subsequently analysed by thermodesorption gas chromatography–mass spectrometry (e.g. Haapanala et al., 2012). Sampling of amines is typically carried out by using impingers, sorbent tubes, acid-coated denuders or solid-phase microextraction (SPME),

while analysis is normally performed by gas chromatography (GC), high-performance liquid chromatography (HPLC) or ion chromatography (IC), all coupled with mass spectrometry (MS) (Parshintsev et al., 2015; Szulejko and Kim, 2014). Most of these techniques require an additional extraction step or/and the use of a derivatization reagent. In addition, the reactivity and adsorption effects associated with small amines are the challenging factors during all analytical steps. VOCs can also be sampled by needle trap microextraction (NTME) that is considered to be more robust than other extraction techniques such as solid-phase microextraction, since the sorbent particles are protected inside the needle (Eom et al., 2008). Furthermore, because NTME is an exhaustive technique, the sensitivity can be improved by increasing the sample volume; and capacity can be expanded by increasing the volume of the sorbent packed in the needle (Eom et al., 2008, 2012). It was demonstrated that NTME was easy, fast and robust in a study on determination of trace amounts of BTEX in water by GC-FID (Jurdáková et al., 2008). The type of adsorbent material (microporous/mesoporous, mechanical/thermal stability) and sampling parameters (such as temperature and sample flow during adsorption) affect the efficiency and reproducibility of adsorption on needle trap devices (Filipiak et al., 2012). For fast in situ analysis, portable gas chromatography–mass spectrometry can be used, which is especially handy when measurements are performed at remote locations (Barreira et al., 2015; Contreras et al., 2008).

In this study, the potential of NTME and portable gas chromatography–mass spectrometry for fast in situ measurement of biogenic and anthropogenic VOCs was evaluated. The results obtained were compared with meteorological data and with particle number concentration at the measurement site.

2 Experimental methods

2.1 Chemicals and materials

CALION™ PV Mix standards, containing 13 compounds adsorbed into a granular solid matrix, were used for performance validation of portable GC–MS. Standard of dimethylamine (DMA) was prepared by diluting dimethylamine hydrochloride (99 %) from Sigma–Aldrich (St. Louis, USA) with ultrapure water (DirectQ-UV, Millipore, USA). A volume of 5 mL was then added to a headspace vial of 20 mL and sealed with an UltraClean 18 mm screw cap with septa (Agilent, Waldbronn, Germany). Sodium hydroxide (0.1 M) from FF-Chemicals Ab (Yli Ii, Finland) was added into the headspace vial with syringe to release DMA into the headspace. (+)-3-Carene ($\geq 98.5\%$) and α -Pinene (98 %) from Sigma–Aldrich (St. Louis, USA), hexanal (98 %), heptanal (98.5 %), octanal (100 %), nonanal (96 %), decanal (96 %) and benzaldehyde (98.5 %) from Accustandard (New Heaven, CT, USA), ethylbenzene (99 %) and

p-xylene ($\geq 99\%$) from Aldrich (Milwaukee, WI), and *m*-xylene ($\geq 99.3\%$) from Merck (Darmstadt, Germany) were used as standards. Pinonaldehyde was synthesized by an oxidative bond cleavage of pinanediol (Sigma Aldrich, St. Louis, USA, 99%) according to the method described by Glasius et al. (1997). SFE-grade CO₂ (AGA, Espoo, Finland) was used for the determination of gas hold-up volume (time) (t_M).

2.2 Measurement site

VOC sampling was made at the SMEAR II station (Station For Measuring Ecosystem-Atmosphere Relations, 61°50.845' N, 24°17.686' E, 179 m above sea level) at Hyytiälä, in southern Finland (Hari and Kulmala, 2005). Tampere, a city with around 200 000 inhabitants, is located 60 km southwest from the SMEAR II station. Major sources of air pollutants from urban areas in Finland include wood combustion and traffic (e.g. Hellén et al., 2008; Taimisto et al., 2011). Flora in Hyytiälä is dominated by Scots pine and Norway spruce approximately 50 years old and with an approximate 18 m canopy height. The sampling place was located about 15 m from a 127 m high mast for atmospheric and flux measurements mounted 2 m above the average forest floor. For the sake of comparison, the sampling system was installed in a fixed place, which was located 30 cm above the ground vegetation and about 3 m from the closest trees. Measurements of temperature and particle number concentration were performed a few meters from the sampling system.

2.3 Sampling and analysis

Samples were collected in mid-summer and autumn 2014. The first part of the sampling campaign occurred from 12 June to 10 July to test the applicability of NTME and portable GC–MS for qualitative and semi-quantitative measurement of VOCs. The second part of the campaign was held from 3 to 12 November to verify the effect of the snow pack on the concentration of VOCs in the air. Sampling was performed by using CUSTODION[®] needle trap microextraction devices (Torion Technologies Inc., Utah, USA). These devices consist of 19-gauge stainless steel needles with a small side-hole for dynamic sampling and packed with Tenax TA (1 mg, 60–80 mesh), Carboxen 1016 (1.6 mg, 60–80 mesh) and Carboxen 1003 (1.5 mg, 60–80 mesh). A needle trap device was installed in a commercial air sampling interface (Fig. S1 in the Supplement) made for needle trap devices (Torion Technologies Inc.). A BUCK EliteTM air sampling pump was used. Besides, a 0.45 µm nylon filter (Nalgene, Rochester, NY) was implemented in the sampling system in order to prevent the blocking of the needle by aerosol particles and other impurities, without compromising the air flow. The air was filtrated through the filter directly into the needle trap device. Analytes were then dynamically extracted

onto the packing material of the needle trap microextraction device. The sampling flow rate and time were 25 mL min⁻¹ and 100 min, respectively. The studied compounds are found in trace levels in ambient air, which requires high sampling volumes to be concentrated. Thus, the breakthrough volume of the needle trap is of concern. Determination of breakthrough volume is challenging as it depends on several conditions such as the type and amount of sorbent materials, the composition and concentration of the sample, temperature and relative humidity (Sanchez, 2014). For some sorbent materials, breakthrough values are given by manufacturers (e.g. <http://www.sisweb.com/index/referenc/resins.htm>). According to these reference values, a sampling volume of 2.5 L is lower than the breakthrough volumes. This was also verified experimentally. One µL of α -pinene was evaporated by heating in a headspace vial (20 mL), from which 0.5 mL of gas phase was transferred with a gas-tight syringe to a Teflon bag (Tedlar[®], 10 L, Sigma Aldrich) filled with nitrogen. Samples of 2, 2.5 and 3 L were collected sequentially by NTME and analysed by portable GC–MS. To ensure sufficient capacity of the sampler and that the breakthrough volume is not reached during sampling of 2.5 L of air, the following study was performed. One µL of α -pinene was evaporated by heating it in a headspace vial (20 mL), from which 0.5 mL of gas phase was transferred with a gas-tight syringe to a Teflon bag (Tedlar[®], 10 L, Sigma Aldrich) filled with nitrogen. The final concentration was 386 ppbV, which is significantly higher than the concentrations usually measured in the ambient air (e.g. Hellén et al., 2004). A sampling kit (Pas Technology, Germany) was used for collection of different volumes of α -pinene from the Tedlar bag into the needle trap device, and samples were analyzed by GC–MS. As can be seen in Fig. S2, a good linearity was observed for all volumes sampled, which strongly suggest that saturation or breakthrough volume was not achieved during the field measurements. A CUSTODION[®] solid phase microextraction syringe (Torion Technologies Inc., Utah, USA) containing a fiber coated with divinylbenzene/polydimethylsiloxane (DVB/PDMS, 65 µm film thickness) was used to obtain retention times and mass spectra for the standards of the analytes tentatively identified with mass spectral library (NIST, 2014) search (National Institute of Standards and Technology, USA, <http://www.nist.gov>). VOCs were analysed on a portable GC–MS (TRIDIONTM-9 Torion Technologies Inc., Utah, USA) consisting of a low thermal mass injector, a low thermal mass capillary gas chromatograph (MXT-5 column, 5 m × 0.1 mm, 0.4 µm film thickness) and a miniature toroidal ion trap mass analyser. A monotherm heatable magnetic stirrer (Variomag Electronicrührer, Labortechnik, Munich, Germany) was used for the heating and stirring of the standards. Air samples were analysed by a similar method to the one described in Barreira et al. (2015). The NTME device was placed into the injection port of the portable GC–MS and the needle trap was exposed during 10 s for thermal desorption. The injector assembly allows for a proper flow of carrier

gas through the side-hole placed above the adsorbent material in the needle trap, which directs the desorbed compounds into the GC column during thermal desorption. Injector and transfer line temperatures were set to 270 °C and ion trap temperature to 150 °C. A 10 : 1 split ratio was applied for 2 s after injection, being increased to 50 : 1 from 10 to 30 s. The temperature program started from 50 °C (10 s), and was increased to 270 °C at 2 °C s⁻¹, and kept at 270 °C until the end of the run. Analytes were ionized by electron ionization (70 eV) and delivered into the mass analyzer, which was set to scan a mass range from 43 to 500 amu. The total run time was 180 s. The carrier gas was helium of 99.996 % purity (AGA, Espoo, Finland). A blank run was performed between each sample collection. For semi-quantitation, extracted ion chromatograms with base ions were used (m/z 93 for Δ^3 -carene and α -pinene; m/z 91 for ethylbenzene, m -xylene and p -xylene, m/z 83 for pinonaldehyde; m/z 105 for benzaldehyde; m/z 56 for hexanal; m/z 55 for heptanal, m/z 69 for octanal; m/z 57 for nonanal and 81 m/z decanal). A conventional GC–MS was also used for laboratory tests. Samples were analyzed with an Agilent 5975 C mass selective detector (Agilent Technologies, Palo Alto, USA). The analytical column used was an InertCap for Amines (30 m \times 0.25 mm (i.d.), GL Sciences, Tokyo, Japan), which was connected to a deactivated fused silica retention gap (1.5 m \times 0.53 mm (i.d.), Agilent Technologies, Palo Alto, USA) with a press-fit connector (BGB Analytik, Bökten, Switzerland). The temperature program consisted of an initial temperature of 40 °C (held for 1 min) being increased at 20 °C min⁻¹ to 250 °C (held for 4.5 min). Helium (99.996 %, AGA, Espoo, Finland) was used as carrier gas in a constant flow mode (1.5 mL min⁻¹). The injection temperature was 250 °C. A splitless mode was used for the lower sampling volumes, while a split of 10 : 1 was applied for the higher volumes collected to prevent saturation of the detector. The GC–MS transfer line temperature was 250 °C, and the ion source and quadrupole temperatures were at 230 and 150 °C, respectively. Electron ionization (70 eV) was used. The mass range was 30–400 m/z .

3 Results

Portable gas chromatography–mass spectrometry method employed in this study has been developed for the analysis of VOCs in our previous research (Barreira et al., 2015). The system was further developed in this work by including needle trap microextraction to allow for a higher VOC-sampling capacity. In contrast to our previous study, where solid-phase microextraction was used, NTME is more robust and enables exhaustive sampling. Minor modifications on the previous method, such as shorter split time, were performed in order to improve sensitivity without compromising the peak shapes. Quantitation was challenging, mainly due to the difficulties in the preparation of gaseous calibration stan-

dards for VOCs at accurate concentrations. For this reason a semi-quantitative approach was used.

Due to small differences in the sampling volume (Tables S1 and S2 in the Supplement) and because breakthrough was not observed for the sampling volume, the peak areas were divided by the volume of air collected to normalize the data. Temperature (measured at 4.2 m height) and particle number concentration (available at <http://avaa.tdata.fi/web/smart>; Junninen et al., 2009) were used for comparison with obtained results, and averaged during the period of sampling. Temperature can influence VOC emissions and thus, must be taken in consideration for the interpretation of results. Between days temperature varied significantly (from 5 to 27 °C). However, during the days, it was almost constant (daily standard deviation less than 4 °C) and its effect can be neglected.

New particle formation events were classified according to Dal Maso et al. (2005), and the classification was further used to evaluate the participation of studied compounds in particle formation and growth events during the first part of the campaign. This classification divided nucleation days into event, non-event and undefined. Event days are those when there is a distinctly new mode of particles starting in the nucleation mode, which prevails and grows over hours. On undefined days, particles are occasionally formed in the nucleation mode range or there is a later phase of a mode growing in the Aitken-mode size range. Non-event days are those where the referred conditions were not observed. A total of 7 event days, 12 undefined event days and 5 non-event days were observed.

3.1 Qualitative analysis

Numerous compounds were tentatively identified from the samples using NIST 2014 spectral library search. Target compounds included monoterpenes, such as α -pinene and Δ^3 -carene, aldehydes, amines and other compounds with recognized relevance for atmospheric physics and chemistry. For the selected compounds, identification was confirmed with authentic standards. Standard samples were prepared by total evaporation of 1 μ L of each standard in a headspace vial, and sequentially diluted by gas-tight syringe to another headspace vials (final concentration 0.15 pL mL⁻¹); collected by SPME (PDMS/DVB, 65 μ m of film thickness) and analysed by portable GC–MS. In contrast, DMA samples were made according to the procedure explained in Sect. 2.1. The retention times and most abundant fragments obtained by portable GC–MS are presented in Table 1. A slight difference in fragmentation was found between the conventional and portable GC–MS, being more expressive for the compounds that are more extensively fragmented. This finding can be explained by the different types of detector used in the portable and conventional GC–MS. The knowledge of the most abundant masses found by portable GC–MS can then be defined as a critical factor during semi-

Table 1. Retention times and most abundant fragments (in order of descending intensity) obtained by portable GC–MS for the identified compounds.

Compound	R.T. (min)	Fragmentation pattern with portable GC–MS	Fragmentation pattern obtained from NIST library
Monoterpenes			
α -Pinene	0.82	93 (100), 92, 91, 53, 79	93 (100), 91, 92, 39, 77
Δ^3 -Carene	0.93	93 (100), 91, 79, 92, 80	93 (100), 91, 92, 39, 77
Aldehydes			
Benzaldehyde	0.87	105 (100), 53, 107, 106, 77	77 (100), 106, 105, 51, 50
Hexanal	0.60	56 (100), 57, 67, 83, 72	44 (100), 56, 41, 43, 57
Heptanal	0.76	55 (100), 71, 97, 70, 44	70 (100), 41, 44, 43, 55
Octanal	0.91	69 (100), 111, 57, 67, 56	43 (100), 44, 41, 56, 84
Nonanal	1.05	57 (100), 143, 67, 69, 81	57 (100), 41, 43, 56, 44
Decanal	1.19	81 (100), 67, 83, 69, 57	43 (100), 41, 57, 55, 44
Pinonaldehyde	1.30	151 (100), 83, 107, 97, 109	83 (100), 69, 43, 98, 55
BTEX			
Ethylbenzene	0.70	91 (100), 106, 92, 78, 65	91 (100), 106, 51, 65, 77
<i>p</i> -Xylene	0.72	91 (100), 106, 105, 79, 119	91 (100), 106, 105, 77, 51
<i>m</i> -Xylene	0.72	91 (100), 106, 105, 107, 65	91 (100), 106, 105, 77, 51
Amines			
Dimethylamine	0.17*	44 (100), 46, 45, 43, 42	44 (100), 45, 28, 42, 43

* no retention in the column ($t_M = 0.12$ min).

quantitative/quantitative analysis of compounds with high fragmentation. Thus, the use of standards during qualitative analysis allowed the proper identification of compounds with different properties by NTME and portable GC–MS.

3.2 VOCs in air samples

Monoterpenes and their oxidation products are an important group of compounds that can participate in aerosol formation and growth (e.g. Spracklen et al., 2006). In this study, α -pinene, Δ^3 -carene and pinonaldehyde were measured by NTME–GC–MS (more detailed information can be found in Table S1). First two compounds have been reported as the main emitted monoterpenes at the boreal forest of Hyttiälä (e.g. Yassaa et al., 2012). Figure 1 shows the comparison between measured amounts of α -pinene, Δ^3 -carene and pinonaldehyde. Temperature was included for the comparison, since temperature dependent emissions have been reported in many previous studies (e.g. Tarvainen et al., 2005). This phenomenon was also observed here because a significant increase in temperature was followed by an increase in the amount of measured monoterpenes in the air. A similar trend on the amounts of α -pinene and Δ^3 -carene was observed, which can be explained by the fact that these compounds are both emitted by *Pinus sylvestris*, the dominant tree species at Hyttiälä boreal forest (Rinne et al., 2000). The results are also consistent with a previous study performed by the same

type of NTME devices and portable GC–MS, used for the in situ headspace collection and analysis of volatiles from varying yellow star-thistle flower heads, sealed in a modified scintillation vial collection apparatus (Beck et al., 2015).

Among the major gaseous oxidation products of α -pinene, only pinonaldehyde was observed. This was due to its vapour pressure that is higher than that of other oxidation products such as pinonic acid, which are more likely to be in the particulate phase. A moderate correlation coefficient (0.52) was found between α -pinene and pinonaldehyde. This result was expected, since an increase in the amount of precursor compounds results in higher output of oxidation products, when optimum conditions that favour the reaction are met. However, pinonaldehyde was detected only in a few samples. For that reason, further development to increase sensitivity of the method is still required. The importance of α -pinene, Δ^3 -carene and pinonaldehyde for atmospheric particle formation and growth has been emphasized also in previous studies, revealing the need for continuous measurement (e.g. Kavouras et al., 1998).

Aldehydes form a class of compounds with a remarkable importance to atmospheric chemistry, due to their photolytic reactions in the atmosphere and contribution to new particle formation (e.g. Jang and Kamens, 2001). As shown in Fig. 2, several aldehydes were found in the samples, in particular hexanal, heptanal, octanal, nonanal, decanal and benzaldehyde (more detailed information can be found on

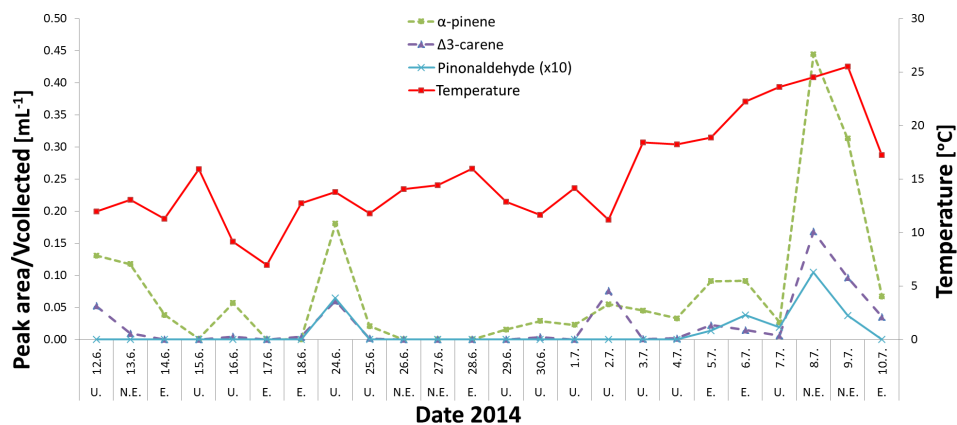


Figure 1. Comparison between the daily average amounts (peak areas/Vcollected) of α -pinene, Δ^3 -carene and pinonaldehyde (Note the different scale for pinonaldehyde (10x)) collected by NTME and analysed by portable GC–MS in mid-summer 2014. (E. corresponds to a day when a nucleation event was observed, U. to an undefined event and N.E. to a day without nucleation events).

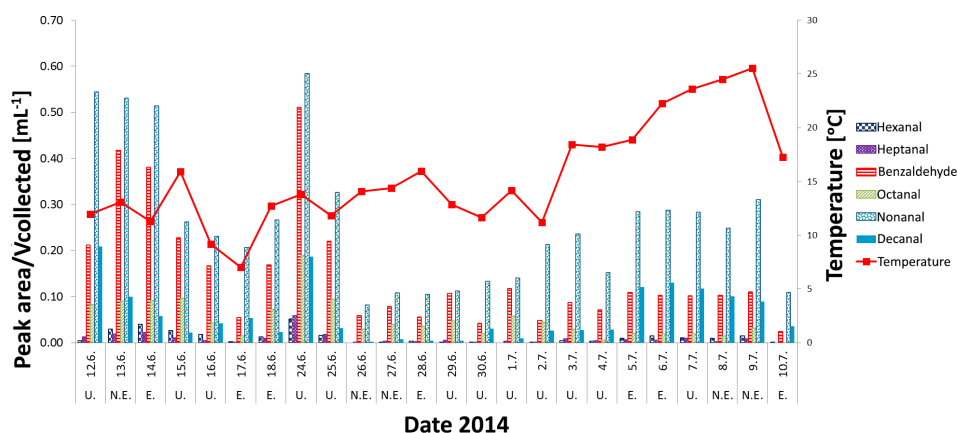


Figure 2. Daily average amounts (peak areas/Vcollected) of aldehydes collected by NTME and analysed by portable GC–MS in mid-summer 2014 (E. corresponds to a day when a nucleation event was observed, U. to an undefined event and N.E. to a day without nucleation events).

Table S2). These compounds were also found in another study performed in the boreal forest of Hyytiälä. The authors used C₁₈-cartridges coated with 2,4-dinitrophenylhydrazine (DNPH) for collection and LC–MS analysis (Hellén et al., 2004) of aldehydes in the air to evaluate the effect of temperature on their amount. However, the temperature effect in our study cannot explain the variance. Instead, diversity of factors, which can also influence the emission of VOCs, are most likely the reason. The correlation between aldehydes, including pinonaldehyde, was evaluated. A good correlation was found between some studied aldehydes (Table S3). The results suggest that these aldehyde emissions originate from the same source. Pinonaldehyde, as an exception, is indicative of a distinct and well known formation source consisting of the α -pinene atmospheric oxidation. Because other aldehydes are not formed as a result of oxidative processes in the air, their common source is most probably associated with the vegetation itself. Aldehyde emission from vegetation has been found in other studies (e.g. Wildt et al., 2003) also, us-

ing similar NTME devices and portable GC–MS (Beck et al., 2015).

Ethylbenzene and *p*- and *m*-xylenes were also identified in the collected samples (Fig. 3, for more detailed information Table S1). These anthropogenic SOA precursors can be important to boreal forest environment and, in addition, they are considered harmful for human health and vegetation, and they can interfere with natural atmospheric processes (e.g. Paralovo et al., 2016). Air mass origins were determined using the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (Stein et al., 2015). These compounds were mainly transported from cities such as Tampere with relevant anthropogenic activity (e.g. Fig. S3a). On the other hand, no pollution events were observed during the days when the wind was coming from geographic coordinates that are relatively pristine, compared to the referred cities, such as the regions located in the north of Finland (e.g. Fig. S3b). More investigation about the effect of these compounds on the climate is still needed, and the method used in

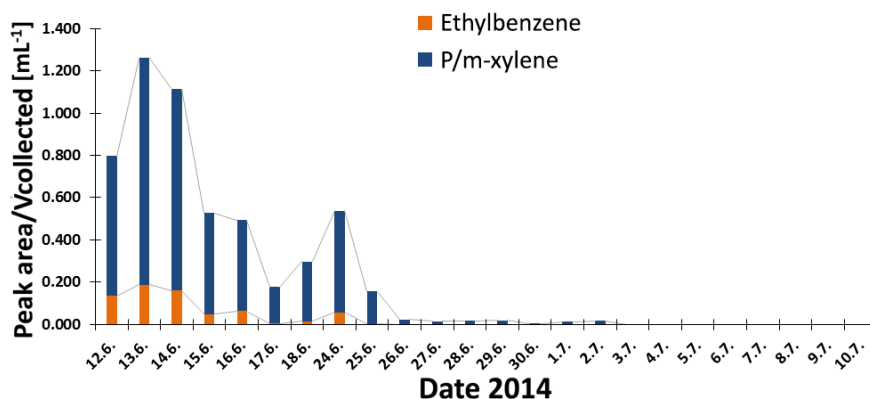


Figure 3. Occurrence of pollution events during the summer campaign, 2014. Ethylbenzene and *p/m*-xylene were identified and monitored by NTME and portable GC–MS during the campaign period.

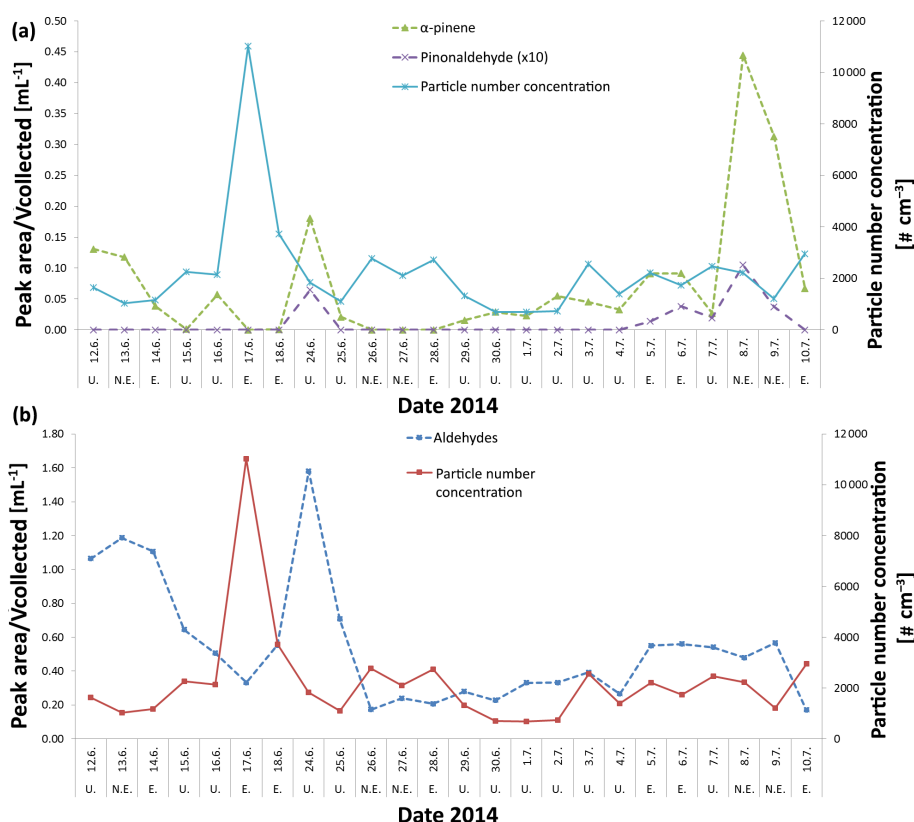


Figure 4. Comparison between the particle number concentration (\# cm^{-3}) and the daily average amounts (peak areas/ $V_{\text{collected}}$) of α -pinene, pinonaldehyde (a), and the sum of aldehydes (benzaldehyde, hexanal, heptanal, octanal, nonanal, and decanal) (b) collected by NTME and analysed by portable GC–MS in mid-summer 2014. (E. corresponds to a day when a nucleation event was observed, U. to an undefined event and N.E. to a day without nucleation events).

this study can constitute an easy alternative and/or a complementary system to conventional methods. However, a better separation of these compounds is required for quantitative purposes, and the use of another chromatographic column should be considered for improvement of the resolution.

Dimethylamine (DMA) was tentatively identified in this study. Characteristic ions and retention time similar to that obtained for standard were found with the method used. However, without almost any retention in the column, and due to possible chromatographic overlapping with ethy-

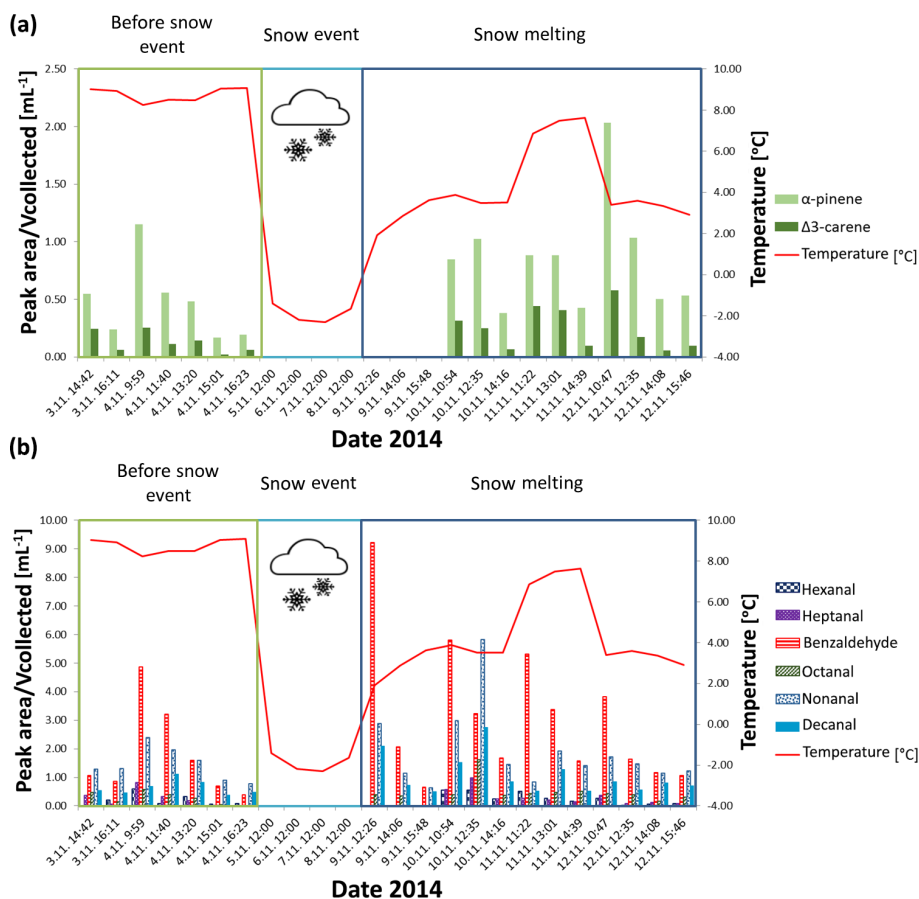


Figure 5. Observation of an increase in monoterpene (a) and aldehyde (b) atmospheric amounts during a snow melt event in November 2014 (daily average temperatures were used on days when sampling was not performed).

lamine (EA) and/or CO_2 , further development of the method for their analysis is still needed.

3.3 VOCs and particle number concentration

The influence of BVOCs on new particle formation was evaluated in this study. The type of nucleation event and particle number concentration were considered in the evaluation. As demonstrated in Fig. 4, particle number concentration was significantly higher during event days when compared to undefined and non-event days. However, the amounts of monoterpenes and pinonaldehyde (amounts were multiplied by a factor of 10 for a better visualization) were lower during days when particle number concentration increased (Fig. 4a). This observation clearly indicates the oxidation of monoterpenes and subsequent partition of their oxidation products in particulate phase. Also, aldehyde concentrations were lower when particle number concentration was higher (Fig. 4b). This evidence was expected since aldehydes can also contribute to new particle formation and growth (e.g. Jang and Kamens, 2001). Altogether, our findings do not contradict with other studies that demonstrated the participa-

tion of VOCs in atmospheric particle formation and growth (e.g. Laaksonen et al., 2008).

3.4 VOCs during a snow melt event

The amounts of biogenic volatile compounds at the SMEAR II were studied by NTME–GC–MS before a soil snow coverage and when snow melted in November. The purpose of the study was to understand how this phenomena affect the concentrations of the atmospheric BVOCs. Also, it can influence the measured atmospheric levels of the studied compounds at soil level.

Figure 5 shows the atmospheric amounts of monoterpene and aldehydes during the snow episode. Monoterpenes, and in particular α -pinene and Δ^3 -carene, were found in small amounts in the beginning of the campaign before the snow event, as expected during this time of the year at the boreal forest site. Temperature was higher during the first part of the campaign, indicating more favourable conditions for higher monoterpene amounts when compared to colder days, as previously described in other studies (e.g. Song et al., 2014; Tingey et al., 1980). During the snow event, no measurements were performed due to technical limitations (needle

trap could freeze and block). On the 9 November, when the temperature raised above 0 °C, monoterpenes were still not found, but they increased rapidly on the 10 November during the snow melt overcoming the amounts found before the snow at higher temperatures. Altogether, these observations suggest the accumulation of these compounds under or into the snow pack. The same phenomena have been verified in another study (Aaltonen et al., 2012). A similar comparison was performed for aldehydes identified and measured in the same sampling period. For the comparison, all identified aldehydes during the autumn campaign were considered. Once more, aldehydes were found in lower amounts during the beginning of the campaign when the temperature was higher. After the snow melt, concentrations of aldehydes increased significantly, reaching levels that overcome the amounts found in the warmest period of the November campaign. This evidence reveals the occurrence of an analogous phenomenon as the one observed for monoterpenes, suggesting that not only monoterpenes but also other BVOCs may undergo an accumulation in the snow pack during snow fall, being released when snow melts. The pool storage of these compounds can be particularly important in spring, when nucleation events are more frequent (e.g. Dal Maso et al., 2005). A snow accumulation of BVOCs during winter and their subsequent release during spring time could contribute significantly to new secondary organic aerosol formation by photo-oxidative processes, which reinforces the interest of studying further these phenomena.

4 Conclusion

VOCs were collected at the boreal forest (SMEAR II, Hyytiälä, Finland) by NTME, and analysed by portable GC–MS. Neither additional sampling line nor sample pretreatment was needed, which reduced analysis time, sample contamination and potential losses during analytical process. The most abundant monoterpenes, pinonaldehyde and aldehydes were successfully measured. The amounts of monoterpenes and aldehydes seem to be lower during days when particle formation was more prone to happen. Ethylbenzene, *p*- and *m*-xylene were also measured, when wind direction was from the cities with significant anthropogenic activity. Increased monoterpene and aldehyde amounts were verified after a snow melt event, revealing their accumulation under or into the snow pack. Results demonstrated the potential of the method for the rapid in situ sampling and analysis of volatile organic compounds in the atmosphere, which can be favourable for the chemical characterization of atmosphere at remote places. Semi-quantitative approach proved to be promising, but quantification with the method developed, including determination of breakthrough volume and addition of internal standard, requires additional studies.

5 Data availability

All data used in the publication are given in the Supplement to this article and can be used by third parties.

The Supplement related to this article is available online at doi:10.5194/amt-9-3661-2016-supplement.

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References

- Aaltonen, H., Pumpanen, J., Hakola, H., Vesala, T., Rasmus, S., and Bäck, J.: Snowpack concentrations and estimated fluxes of volatile organic compounds in a boreal forest, *Biogeosciences*, 9, 2033–2044, doi:10.5194/bg-9-2033-2012, 2012.
- Altomose, B., Gong, J., Zhu, T., Hu, M., Zhang, L., Cheng, H., Zhang, L., Tong, J., Kipen, H. M., and Ohman-Strickland, P.: Aldehydes in relation to air pollution sources: A case study around the Beijing Olympics, *Atmos. Environ.*, 109, 61–69, doi:10.1016/j.atmosenv.2015.02.056, 2015.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.*, 34, 2063–2101, doi:10.1016/S1352-2310(99)00460-4, 2000.
- Barreira, L., Parshintsev, J., Kärkkäinen, N., Hartonen, K., Jussila, M., Kajos, M., Kulmala, M., and Riekkola, M.-L.: Field measurements of biogenic volatile organic compounds in the atmosphere by dynamic solid-phase microextraction and portable gas chromatography-mass spectrometry, *Atmos. Environ.*, 115, 214–222, doi:10.1016/j.atmosenv.2015.05.064, 2015.
- Beck, J. J., Porter, N., Cook, D., Gee, W. S., Griffith, C. M., Rands, A. D., Truong, T. V., Smith, L., and San Román, I.: In-field volatile analysis employing a hand-held portable GC-MS: emission profiles differentiate damaged and undamaged yellow starthistle flower heads, *Phytochem. Anal.*, 26, 395–403, doi:10.1002/pca.2573, 2015.
- Bäck, J., Aalto, J., Henriksson, M., Hakola, H., He, Q., and Boy, M.: Chemodiversity of a Scots pine stand and implications for terpene air concentrations, *Biogeosciences*, 9, 689–702, doi:10.5194/bg-9-689-2012, 2012.

- Chen, M., Titcombe, M., Jiang, J., Jen, C., Kuang, C., Fischer, M. L., Eisele, F. L., Siepmann, J. I., Hanson, D. R., and Zhao, J.: Acid–base chemical reaction model for nucleation rates in the polluted atmospheric boundary layer, *PNAS*, 109, 18713–18718, doi:10.1073/pnas.1210285109, 2012.
- Contreras, J. A., Murray, J. A., Tolley, S. E., Oliphant, J. L., Tolley, H. D., Lammert, S. A., Lee, E. D., Later, D. W., and Lee, M. L.: Hand-portable gas chromatograph-toroidal ion trap mass spectrometer (GC-TMS) for detection of hazardous compounds, *J. Am. Soc. Mass. Spectrom.*, 19, 1425–1434, doi:10.1016/j.jasms.2008.06.022, 2008.
- Dal Maso, M., Kulmala, M., Riipinen, I., Wagner, R., Hussein, T., Aalto, P. P., and Lehtinen, K. E.: Formation and growth of fresh atmospheric aerosols: eight years of aerosol size distribution data from SMEAR II, Hyytiälä, Finland, *Boreal Environ. Res.*, 10, 323–336, 2005.
- Eom, I.-Y., Tugulea, A.-M., and Pawliszyn, J.: Development and application of needle trap devices, *J. Chromatogr. A*, 1196, 3–9, doi:10.1016/j.chroma.2008.02.090, 2008.
- Eom, I.-Y., Risticvic, S., and Pawliszyn, J.: Simultaneous sampling and analysis of indoor air infested with *Cimex lectularius* L. (Hemiptera: Cimicidae) by solid phase microextraction, thin film microextraction and needle trap device, *Anal. Chim. Acta*, 716, 2–10, doi:10.1016/j.aca.2011.06.010, 2012.
- Filipiak, W., Filipiak, A., Ager, C., Wiesenhofer, H., and Amann, A.: Optimization of sampling parameters for collection and pre-concentration of alveolar air by needle traps, *J. Breath Res.*, 6, 027107, doi:10.1088/1752-7155/6/2/027107, 2012.
- Glasius, M., Calogirou, A., Jensen, N., Hjorth, J., and Nielsen, C.: Kinetic study of gas-phase reactions of pinonaldehyde and structurally related compounds, *Int. J. Chem. Kinet.*, 29, 527–533, doi:10.1002/(SICI)1097-4601(1997)29:7<527::AID-KIN7>3.0.CO;2-W, 1997.
- Haapanala, S., Hakola, H., Hellén, H., Vestenius, M., Levula, J., and Rinne, J.: Is forest management a significant source of monoterpenes into the boreal atmosphere?, *Biogeosciences*, 9, 1291–1300, doi:10.5194/bg-9-1291-2012, 2012.
- Hao, L. Q., Yli-Pirilä, P., Tiitta, P., Romakkaniemi, S., Vaattovaara, P., Kajos, M. K., Rinne, J., Heijari, J., Kortelainen, A., Miettinen, P., Kroll, J. H., Holopainen, J. K., Smith, J. N., Joutsensaari, J., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: New particle formation from the oxidation of direct emissions of pine seedlings, *Atmos. Chem. Phys.*, 9, 8121–8137, doi:10.5194/acp-9-8121-2009, 2009.
- Hari, P. and Kulmala, M.: Station for measuring ecosystem-atmosphere relations, *Boreal Environ. Res.*, 10, 315–322, 2005.
- Hellén, H., Hakola, H., Reissell, A., and Ruuskanen, T. M.: Carbonyl compounds in boreal coniferous forest air in Hyytiälä, Southern Finland, *Atmos. Chem. Phys.*, 4, 1771–1780, doi:10.5194/acp-4-1771-2004, 2004.
- Hellén, H., Hakola, H., Haaparanta, S., Pietarila, H., and Kauhaniemi, M.: Influence of residential wood combustion on local air quality, *Sci. Total Environ.*, 393, 283–290, doi:10.1016/j.scitotenv.2008.01.019, 2008.
- Jang, M. and Kamens, R. M.: Atmospheric secondary aerosol formation by heterogeneous reactions of aldehydes in the presence of a sulfuric acid aerosol catalyst, *Environ. Sci. Technol.*, 35, 4758–4766, doi:10.1021/es010790s, 2001.
- Junninen, H., Lauri, A., Keronen, P., and Aalto, P.: Smart-SMEAR: on-line data exploration and visualization tool for SMEAR stations, *Boreal Environ. Res.*, 14, 447–457, 2009.
- Jurdáková, H., Kubinec, R., Jurčišinová, M., Krkošová, Ž., Blaško, J., Ostrovský, I., Soják, L., and Berezkin, V. G.: Gas chromatography analysis of benzene, toluene, ethylbenzene and xylenes using newly designed needle trap device in aqueous samples, *J. Chromatogr. A*, 1194, 161–164, doi:10.1016/j.chroma.2008.04.065, 2008.
- Kavouras, I. G., Mihalopoulos, N., and Stephanou, E. G.: Formation of atmospheric particles from organic acids produced by forests, *Nature*, 395, 683–686, doi:10.1038/27179, 1998.
- Kieloaho, A.-J., Hellén, H., Hakola, H., Manninen, H. E., Nieminen, T., Kulmala, M., and Pihlatie, M.: Gas-phase alkylamines in a boreal Scots pine forest air, *Atmos. Environ.*, 80, 369–377, doi:10.1016/j.atmosenv.2013.08.019, 2013.
- Kourtchev, I., Ruuskanen, T., Keronen, P., Sogacheva, L., Dal Maso, M., Reissell, A., Chi, X., Vermeylen, R., Kulmala, M., and Maenhaut, W.: Determination of isoprene and α - β -pinene oxidation products in boreal forest aerosols from Hyytiälä, Finland: diel variations and possible link with particle formation events, *Plant Biol.*, 10, 138–149, doi:10.1055/s-2007-964945, 2008.
- Kulmala, M.: How particles nucleate and grow, *Science*, 302, 1000–1001, doi:10.1126/science.1090848, 2003.
- Kulmala, M., Kontkanen, J., Junninen, H., Lehtipalo, K., Manninen, H. E., Nieminen, T., Petäjä, T., Sipilä, M., Schobesberger, S., and Rantala, P.: Direct observations of atmospheric aerosol nucleation, *Science*, 339, 943–946, doi:10.1126/science.1227385, 2013.
- Kurtén, T., Loukonen, V., Vehkamäki, H., and Kulmala, M.: Amines are likely to enhance neutral and ion-induced sulfuric acid-water nucleation in the atmosphere more effectively than ammonia, *Atmos. Chem. Phys.*, 8, 4095–4103, doi:10.5194/acp-8-4095-2008, 2008.
- Laaksonen, A., Kulmala, M., O’Dowd, C. D., Joutsensaari, J., Vaattovaara, P., Mikkonen, S., Lehtinen, K. E. J., Sogacheva, L., Dal Maso, M., Aalto, P., Petäjä, T., Sogachev, A., Yoon, Y. J., Lihavainen, H., Nilsson, D., Facchini, M. C., Cavalli, F., Fuzzi, S., Hoffmann, T., Arnold, F., Hanke, M., Sellegri, K., Umann, B., Junkermann, W., Coe, H., Allan, J. D., Alfarra, M. R., Worsnop, D. R., Riekkola, M.-L., Hyötyläinen, T., and Viisanen, Y.: The role of VOC oxidation products in continental new particle formation, *Atmos. Chem. Phys.*, 8, 2657–2665, doi:10.5194/acp-8-2657-2008, 2008.
- Li, K., Wang, W., Ge, M., Li, J., and Wang, D.: Optical properties of secondary organic aerosols generated by photooxidation of aromatic hydrocarbons, *Sci. Rep.*, 4, 4922, doi:10.1038/srep04922, 2014.
- Nölscher, A. C., Williams, J., Sinha, V., Custer, T., Song, W., Johnson, A. M., Axinte, R., Bozem, H., Fischer, H., Pouvesle, N., Phillips, G., Crowley, J. N., Rantala, P., Rinne, J., Kulmala, M., Gonzales, D., Valverde-Canossa, J., Vogel, A., Hoffmann, T., Ouwersloot, H. G., Vilà-Guerrou de Arellano, J., and Lelieveld, J.: Summertime total OH reactivity measurements from boreal forest during HUMPPA-COPEC 2010, *Atmos. Chem. Phys.*, 12, 8257–8270, doi:10.5194/acp-12-8257-2012, 2012.
- Paralovo, S. L., Borillo, G. C., Barbosa, C. G., Godoi, A. F. L., Yamamoto, C. I., de Souza, R. A., Andreoli, R. V., Costa, P. S., Almeida, G. P., and Manzi, A. O.: Observations of atmospheric

- monoaromatic hydrocarbons at urban, semi-urban and forest environments in the Amazon region, *Atmos. Environ.*, 128, 175–184, doi:10.1016/j.atmosenv.2015.12.053, 2016.
- Parshintsev, J., Rönkkö, T., Helin, A., Hartonen, K., and Riekkola, M.-L.: Determination of atmospheric amines by on-fiber derivatization solid-phase microextraction with 2, 3, 4, 5, 6-pentafluorobenzyl chloroformate and 9-fluorenylmethoxycarbonyl chloride, *J. Chromatogr. A*, 1376, 46–52, doi:10.1016/j.chroma.2014.12.040, 2015.
- Reinhardt, A., Emmenegger, C., Gerrits, B., Panse, C., Dommen, J., Baltensperger, U., Zenobi, R., and Kalberer, M.: Ultrahigh mass resolution and accurate mass measurements as a tool to characterize oligomers in secondary organic aerosols, *Anal. Chem.*, 79, 4074–4082, doi:10.1021/ac062425v, 2007.
- Rinne, J., Hakola, H., Laurila, T., and Rannik, Ü.: Canopy scale monoterpene emissions of *Pinus sylvestris* dominated forests, *Atmos. Environ.*, 34, 1099–1107, doi:10.1016/S1352-2310(99)00335-0, 2000.
- Rinne, J., Bäck, J., and Hakola, H.: Biogenic volatile organic compound emissions from the Eurasian taiga: current knowledge and future directions, *Boreal Environ. Res.*, 14, 807–826, 2009.
- Sanchez, J. M.: Effects of packing density, flow and humidity on the performance of needle trap devices, *J. Chromatogr. A*, 1369, 18–25, doi:10.1016/j.chroma.2014.09.081, 2014.
- Scheff, P. A. and Wadden, R. A.: Receptor modeling of volatile organic compounds. 1. Emission inventory and validation, *Environ. Sci. Technol.*, 27, 617–625, doi:10.1021/es00041a005, 1993.
- Seinfeld, J. H. and Pankow, J. F.: Organic atmospheric particulate material, *Annu. Rev. Phys. Chem.*, 54, 121–140, doi:10.1146/annurev.physchem.54.011002.103756, 2003.
- Song, W., Staudt, M., Bourgeois, I., and Williams, J.: Laboratory and field measurements of enantiomeric monoterpene emissions as a function of chemotype, light and temperature, *Biogeosciences*, 11, 1435–1447, doi:10.5194/bg-11-1435-2014, 2014.
- Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Mann, G. W., and Sihto, S.-L.: The contribution of boundary layer nucleation events to total particle concentrations on regional and global scales, *Atmos. Chem. Phys.*, 6, 5631–5648, doi:10.5194/acp-6-5631-2006, 2006.
- Stein, A., Draxler, R., Rolph, G., Stunder, B., Cohen, M., and Ngan, F.: NOAA's HYSPLIT atmospheric transport and dispersion modeling system, *B. Am. Meteorol. Soc.*, 96, 2059–2077, doi:10.1175/BAMS-D-14-00110.1, 2015.
- Szulejko, J. E. and Kim, K.-H.: A review of sampling and pretreatment techniques for the collection of airborne amines, *TrAC, Trends Anal. Chem.*, 57, 118–134, doi:10.1016/j.trac.2014.02.010, 2014.
- Taimisto, P., Tainio, M., Karvosenoja, N., Kupiainen, K., Porvari, P., Karppinen, A., Kangas, L., Kukkonen, J., and Tuomisto, J. T.: Evaluation of intake fractions for different subpopulations due to primary fine particulate matter (PM_{2.5}) emitted from domestic wood combustion and traffic in Finland, *Air Qual. Atmos. Health*, 4, 199–209, doi:10.1007/s11869-011-0138-3, 2011.
- Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots pine, *Atmos. Chem. Phys.*, 5, 989–998, doi:10.5194/acp-5-989-2005, 2005.
- Tingey, D. T., Manning, M., Grothaus, L. C., and Burns, W. F.: Influence of light and temperature on monoterpene emission rates from slash pine, *Plant Physiol.*, 65, 797–801, doi:10.1104/pp.65.5.797, 1980.
- Wildt, J., Kobel, K., Schuh-Thomas, G., and Heiden, A.: Emissions of oxygenated volatile organic compounds from plants Part II: emissions of saturated aldehydes, *J. Atmos. Chem.*, 45, 173–196, doi:10.1023/A:1024030821349, 2003.
- Yassaa, N., Song, W., Lelieveld, J., Vanhatalo, A., Bäck, J., and Williams, J.: Diel cycles of isoprenoids in the emissions of Norway spruce, four Scots pine chemotypes, and in Boreal forest ambient air during HUMPPA-COPEC-2010, *Atmos. Chem. Phys.*, 12, 7215–7229, doi:10.5194/acp-12-7215-2012, 2012.
- Yu, H., McGraw, R., and Lee, S. H.: Effects of amines on formation of sub-3 nm particles and their subsequent growth, *Geophys. Res. Lett.*, 39, L02807, doi:10.1029/2011GL050099, 2012.
- Zelenyuk, A., Imre, D., Earle, M., Easter, R., Korolev, A., Leitch, R., Liu, P., Macdonald, A. M., Ovchinnikov, M., and Strapp, W.: In Situ Characterization of Cloud Condensation Nuclei, Interstitial, and Background Particles Using the Single Particle Mass Spectrometer, SPLAT II, *Anal. Chem.*, 82, 7943–7951, doi:10.1021/ac1013892, 2010.