Vertical profiles of volatile organic compounds and fine particles in atmospheric air by using aerial drone with miniaturized samplers and portable devices

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Abstract. The increase of volatile organic compounds (VOCs) emissions released into the atmosphere is one of the main threats to human health and climate. VOCs can adversely affect human life through their contribution to air pollution directly and indirectly by reacting via several mechanisms in the air to form secondary organic aerosols. In this study, aerial drone equipped with miniaturized air sampling systems including up to four solid-phase microextraction (SPME) Arrows and four in-tube extraction (ITEX) samplers for the collection of VOCs, along with portable devices for the real-time measurement of black carbon (BC) and total particle numbers at high altitudes was exploited. In total, 135 air samples were collected under optimal sampling conditions ~~in October 2021~~ from October 4 to October 14, 2021 at the boreal forest SMEAR II Station, Finland. A total of 48 different VOCs, including nitrogen-containing compounds, alcohols, aldehydes, ketones, organic acids, and hydrocarbons, were detected at different altitudes from 50 to 400 m above ground level with the concentrations up to 6898 ng m^{-3} in gas phase and 8613 ng m^{-3} in particle phase. Clear differences in VOCs distribution were seen in samples collected from different altitudes, depending on the VOC sources. It was also possible to collect aerosol particles by the filter accessory attached on the ITEX sampling system, and five dicarboxylic acids were quantified with the concentrations of 0.43 to 10.9 µg m^{-3}. The BC and total particle number measurements provided similar diurnal patterns, indicating

their correlation. For spatial distribution, ~~surprisingly~~ the BC concentrations were increased at higher altitudes being 2278 ng m^{-3} at 100 m and 3909 ng m^{-3} at 400 m. The measurements onboard the drone provided insights into horizontal and vertical variability in BC and aerosol number concentrations above the boreal forest.

Keywords: aerial drone; miniaturized air sampling systems; solid-phase microextraction Arrow; in-tube extraction; volatile organic compounds; black carbon; total particle number.

1. Introduction

The global phenomenon of climate change has attracted a huge attention in the past decades. Atmospheric aerosol particles can influence the climate system directly by scattering sunlight, transmission, and absorption of radiation, and indirectly by acting as nuclei for cloud formation (Hemmilä, 2020; Kim et al., 2017; Oh et al., 2020). Fine aerosol particles have sizes close to the wavelength range of the visible light, and therefore they are expected to have a stronger climatic impact than larger particles (Kanakidou et al., 2005). In addition, the aerosol particles also give an adverse effect on air quality and human health by exposing human's respiratory system to aerosol particulate matter (PM) that can get into lungs and translocate into vital organs due to their tiny size (Fu et al., 2013).

The formation and growth process of aerosol particles have been studied by many research groups (Ahlberg et al., 2017; Camredon et al., 2007; Casquero-Vera et al., 2020; Kulmala et al., 2013, 2014; Peng et al., 2021; Ziemann and Atkinson, 2012). To study the particle formation in the atmosphere, it is important to assess the possible sources of the atmospheric particles, for instance by the presence of volatile organic compounds (VOCs). Hydrocarbons and amines e.g. have been extensively investigated either by modelling or by laboratory chamber experiments to show their contribution to secondary organic aerosol (SOA) formation. These VOCs, along with other thousands of organic gaseous trace species, are directly emitted from biogenic and anthropogenic sources. In the atmosphere, VOCs are oxidized by reactions with atmospheric oxidants such as O_3^-, OH^-, NO_3^- and Cl^- radicals to form less volatile products and further subsequently partition into aerosol particle leading to SOA formation (Almeida et al., 2013; Kulmala et al., 2014; Zahardis et al., 2008; Ziemann and Atkinson, 2012). The SOAs then become the major components of fine aerosol particulate matter, such as PM 10 and PM 2.5 that pollutes the environment (Fermo et al., 2021; Ge et al., 2011; Kulmala et al., 2014).

Another important component that contributes to air pollution is Black Carbon (BC), which is emitted mostly as a byproduct of fossil fuel combustion and biomass burning (Hyvärinen et al., 2011). In addition, industry, energy production, and domestic cooking contribute to the BC in the atmosphere (Kumar et al., 2015). BC has been associated with adverse effects on human health, such as premature mortality, and also on earth temperature and climate, since it absorbs solar radiation very strongly (Anenberg et al., 2012; Jacobson, 2010).

In addition to VOCs and BC, atmospheric organic acids, such as low molecular weight (LMW) dicarboxylic acids are also recognized as ubiquitous aerosol constituents in the urban region. As highly water-soluble compounds they have the capability to significantly enhance the hygroscopicity of aerosol particles (Kanakidou et al., 2005). LMW diacids can be emitted from biomass burning, vehicular exhausts, natural marine, and also produced from the atmospheric photo-oxidation of various organic precursors (Fu et al., 2013; Kawamura and Sakaguchi, 1999; Rinaldi et al., 2011).

The condensation particle counters (CPC) are important devices for the measurement of aerosol number concentrations and aerosol particle fluxes (McMurry, 2000; Kangasluoma and Attoui, 2019; Petäjä et al., 2001). CPCs are commonly used in the ambient air quality monitoring to measure the number concentration of airborne submicron particles with sizes down to a few nanometers (Asbach et al., 2017; Buzorius et al., 1998). The conventional CPCs have generally not been used as portable devices due to their weight and size. However, recently small CPCs are emerging and being deployed for example for vertical profiling on-board drones (Kim et al., 2018; Carnerero et al., 2018), and other platforms (Petäjä et al., 2012).

In our previous research, we used reliable and versatile miniaturized air sampling (MAS) techniques, which have many benefits for on-site sampling, such as small size, low sampling time, environmental friendliness, easy operation and flexibility for practical applications and automation (Lan et al., 2020; Pusfitasari et al., 2022; Ruiz-Jimenez et al., 2019). Solid-phase microextraction (SPME) Arrow and in-tube extraction (ITEX) sampling systems have been successfully employed for the reliable collection of VOCs from ambient air samples (Lan et al., 2019b, a; Pusfitasari et al., 2022). An exhaustive sampling technique ITEX sampling system with large sorbent volume can be fully automated, and it provides continuous air sampling, reliable analysis, and quantification (Lan et al., 2019a; Pusfitasari et al., 2022). As an active sampler, ITEX system allows the simultaneous collection of gas and particle phase compounds. Extra sampling accessories, including adsorbent trap and filter accessories together with ITEX have enhanced the selectivity of the sampling system and allowed the ITEX to collect only gas phase (Pusfitasari et al., 2022). After sample

collection, the compounds were desorbed from the samplers, separated and detected by thermal desorption (TD) gas chromatography-mass spectrometry (GC-MS).

In this study, the sampling of VOCs and measurement of total particle number concentration and Black Carbon (BC) directly at various altitudes, from 50 to 400 m, were performed using an aerial drone as the platform as in our previous research (Lan et al., 2021; Pusfitasari et al., 2022; Ruiz-Jimenez et al., 2019). The sampling platform contained now up to four SPME Arrows and four ITEX units, with additional portable commercial BC device for BC real-time measurement and a lab-made portable CPC for total particle number observation. The compositions of different gas phase fractions collected both by SPME Arrow and ITEX systems, aerosol particles collected by ITEX sampling including filter accessory as well as BC and particle numbers were evaluated at different altitudes and temporal variation at boreal forest SMEAR II Station in October 2021. In addition, the possible correlation between VOCs, BC and total particle number concentrations were also clarified.

2. Materials and methods

2.1. Reagent and materials

Detailed information of reagents used, including their purities, is given in the supplemental information S1.

Empty ITEX units, DVB-PDMS and Carbon coated WR-SPME Arrow systems were purchased from BGB Analytik AG (Zurich, Switzerland). TENAX-GR was purchased from Altech (Deerfield, IL, USA). The mesoporous silica-based materials, the Mobil Composition of Matter No. 41 (MCM-41) and titanium hydrogen phosphate-modified (MCM-41-TP) materials were synthesized via sol-gel template as described in our previous publication (Lan et al., 2019a). The instructions for ITEX packing with 30 mg MCM-41-TP and 60 mg Tenax-GR are described in Lan *et al*. (2019b). The preparation of MCM-41-SPME Arrow with the sorbent thickness of 40 µm and length of 20 mm, is found from Lan *et al* (2019a).

2.2. Instrumentation

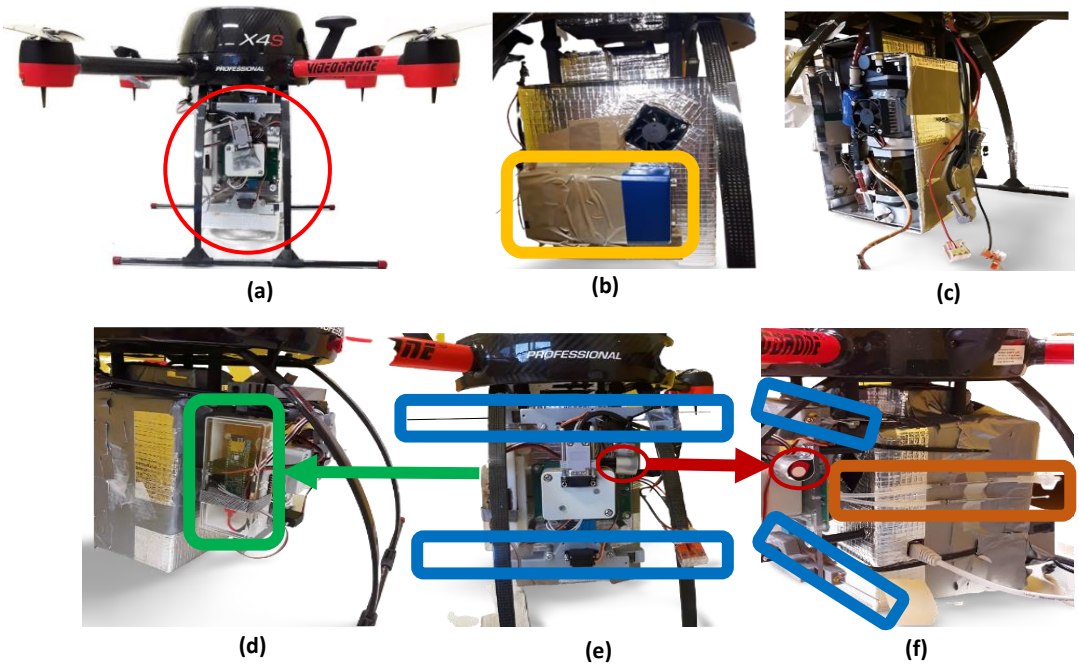
A lab-made permeation system was employed to create an artificial gas-phase sample in the laboratory (Lan et al., 2019a, 2021; Pusfitasari et al., 2022). A PAL Cycle Composer and PAL RTC autosampler that were used for sample collection and desorption in the laboratory were from CTC Analytics (Zwingen, Switzerland). An Agilent 6890N gas chromatograph coupled with an Agilent 5975C mass spectrometer (Agilent Technologies, Pittsburg, PA, USA) was used for the method optimization and quality assurance tests for air samples in the laboratory. For onsite analysis, an Agilent 6890 N gas chromatograph (Agilent Technologies, Pittsburg, PA, USA) equipped with a lab made ITEX heater for thermal desorption was

employed and coupled to an Agilent 5973 mass spectrometer. The GC capillary column used for the chromatographic separations was an InertCap™ for amines (30 m length x 0.25 mm i.d., without any information for the film thickness, GL Sciences, Tokyo, Japan).

For organic acid determination, an Agilent 1260 Infinity high performance liquid chromatography (HPLC) system equipped with a binary pump, autosampler, degassing unit, and a column compartment was employed and coupled to an Agilent 6420 triple-quadrupole mass spectrometer with electrospray ion source (ESI) (Agilent Technologies, Palo Alto, CA, USA). Chromatographic separations were performed with a 2.1x150 mm SeQuant ®ZIC®-cHILIC (3 µm particle size) hydrophilic interaction liquid chromatography (HILIC) column (MerckKGaA, Darmstadt, Germany). A KrudKatcher ULTRA HPLC in-line filter (0.5 µm) from Phenomenex Inc (Torrance, CA, USA) protected the column from particulate impurities.

2.3. **Drone platform construction**

A remote-controlled Geodrone X4L (Videodrone, Finland), similar to that used in our previous studies (Lan et al., 2021; Pusfitasari et al., 2022) with some modifications, was employed to carry out miniaturized air sampling and analysis systems. With the dimension of 58x58x37 cm (width x depth x height), it could carry the modified sampling box including our MAS system (up to four SPME Arrow units and up to four ITEXs) with a new, light sampling pump for ITEX system. In addition, some portable devices were also attached to the drone to measure Black Carbon (BC) and particle sizes by condensation particle counter (CPC). BC portable device in the field was an AethLabs AE51-S6-1408, with the application version of 2.2.4.0 (San Francisco, CA, USA). It was operated at 880 nm wavelength, with the air flowrate of 99 mL/min. The portable CPC was a laboratory-made. The portable CPC measured total aerosol particle number concentration between sizes from 20 nm and 5 µm. The references for BC and particle concentrations were measured at Boreal forest SMEAR II Station at the altitude of 4 meters by an AE33 (operated at 880 nm) and an aerosol electrometer (TSI 3772), respectively.



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145 **Figure 1.** Drone platform sampling system with: **(a)** Air sampling box carried by aerial drone. **(b)** BC placed
146 behind the box. **(c)** CPC inserted into the sampling box. **(d)** The right side of the sampling box is a sensor
147 that measured temperature and relative humidity. **(e)** Front position of the sampling box consisted of SPME
148 Arrow units (marked with blue) and a VOC sensor (red circle). **(f)** Sides of the sampling box included ITEX
149 unit and filter accessory (brown).

150 2.4. **Gas chromatography-mass spectrometry analysis**

151 The SPME Arrow and ITEX sampling systems were preconditioned at 250 °C for 10 min under inert gas N_2.
152 Prior to sampling, decafluorobiphenyl vapor (as an internal standard) was spiked to SPME Arrow and ITEX
153 for 1 min and 5 mL, respectively. After sampling, the SPME Arrow unit was injected to the GC inlet to
154 desorb the analytes at the temperature of 250 °C for 1 min. While for ITEX, 800 µL of He was aspirated to
155 the ITEX syringe, and the analytes were desorbed at the temperature of 250°C and injected into the GC-MS
156 system by moving the plunger down with the injection speed of 200 µL s^{-1}. All the analyses were done in
157 splitless injection at 250 ˚C. For chromatographic separations, the GC oven temperature was programmed
158 from 40 °C (held for 2 min) to 250 °C (held for 10 min) at a rate of 20 °C min^{-1}. The temperature of transfer
159 line, ion source and quadrupole were 250, 230 and 150 °C, respectively. Electron ionization (EI) mode (70
160 eV) was used, and the scan range was from m/z 15 to 350. Helium (99.996 %, AGA, Espoo, Finland) was
161 used as a carrier gas at a constant flow rate of 1.2 mL min^{-1}.

2.5. Hydrophilic Interaction liquid chromatography-tandem mass spectrometry method for organic acids analysis

Acetonitrile (ACN) was used as the main organic solvent containing 0.01 % formic acid (FA) (as Eluent A), while Eluent B is aqueous 0.01 % FA solution. The applied LC gradient was the following: 5 % B (0-6 min), 5 to 20 % B (5-18 min), and post run for 15 min. The flow rate for the analysis was 0.25 mL min^{-1} and column temperature was maintained at 40 °C. The injection volume was 10 µl. The LC system was coupled to the triple quadrupole mass spectrometer equipped with ESI. The ion source was operated in both positive and negative modes.

2.6. Method development, quality control and quality assurance studies.

The optimization study for MCM-41-TP-ITEX system, including optimization of the adsorption and desorption processes, sampling kinetics, breakthrough volume, and the recovery of the storage time, has been carried out in our previous study using multivariate analysis (Pusfitasari et al., 2022). The evaluation and validation of SPME Arrow units coated with MCM-41, DVB-PDMS, and carbon wide range (Carbon WR) for the sampling of VOCs have also been studied in our previous research (Helin et al., 2015; Lan et al., 2019b).

For TENAX-GR-ITEX sampler, the same method development and validation including the determination of optimum flow rate, repeatability, reproducibility, and sample storage were done by using our laboratory-made autosampler. The repeatability and reproducibility of TENAX-GR-ITEX system were studied by analyzing the model compounds with five different ITEX units five times, each. The sampling flow rate (47 mL min^{-1}) was measured at least once for each ITEX during the comparison.

The storage study was performed by keeping the TENAX-GR-ITEX system at room temperature and in a freezer (-20 °C). The purpose was to monitor how conditions affect the adsorption of chemicals in surrounding environment to TENAX-GR during storage. The retainment of adsorbed analytes in different conditions was also monitored. The difference in recovery between control sample (not stored) and stored sample was regarded as the loss of the compound.

2.7. Application, measurement sites and sample collection in the field

The field sampling was carried out at the SMEAR II Station (Station for Measuring Ecosystem–Atmosphere Relations; (Hari and Kulmala, 2005), with the coordinate of 61.84263˚ N - 24.29013˚ E), Hyytiälä, from 4 to

14 October 2021. As many as 53 drone flights were performed and 135 air samples in total were collected (67 samples were collected using ITEX and 68 using SPME Arrow sampling systems). Table 1 shows the summary of sampling and measurement techniques used in this study.

SPME Arrow units with different coating materials, DVB/PDMS, MCM-41, Carbon WR, were exploited to collect gas phase samples. MCM-41-TP-ITEX and TENAX-GR-ITEX sampling systems were used to simultaneously collect gas phase and particles. In the field study, the measured ITEX airflow ranged from 40 to 78 mL min^{-1}. The flow was carefully measured before the sampling and after analyte desorption. ITEX sampling volumes were then obtained by multiplying the value of ITEX airflow rate with the sampling time. Other sampling variables, such as sampling location, remained constant.

To study the average composition of VOCs in the atmosphere (Section 3.3), the samples were collected simultaneously by ITEX and SPME Arrow systems located on the drone at the altitudes from 50 m to 400 m. Composition samples were collected for 2 min at each altitude and during the descending of the drone by starting at the highest altitude of 400, followed by 300, 200, 100 and 50 m (Supplemental Fig. S1). In this case, a total sampling time was 13-14 min (consist of total of 10 min at different altitudes, and 3-4 minutes when the drone was descending from 400 m to 50 m), with a total flight time close to 20 min including take-off and landing.

The VOC composition at the altitudes of 50 m and 400 m was also separately determined (Section 3.6). Detail schematic picture on our sampling system is seen in the Supplemental Fig. S2 (sampling at 50 m for 10 min) and Supplemental Fig. S3 (sampling at 400 m for 10 min).

Evaluation of ITEX sampling with filter accessory was also studied (Section 3.4). TENAX-GR-ITEX furnished with filter accessory was employed to collect the gas phase only. A polytetrafluoroethylene (PTFE) filter with the pore size of 0.2 μm (diameter of 13 mm, VWR) was used as ITEX filter accessory to remove aerosol particles from the natural air samples. The results obtained were directly compared with those achieved by Carbon WR-SPME Arrow sampling system. The recovery was calculated from the difference between concentrations obtained by SPME Arrow and by ITEX furnished with filter accessory. Details about the experiments, sampling time and altitudes are found from Supplemental Fig. S1.

Suitability of particle trap for subsequent analysis was evaluated by the determination of the organic acids retained or adsorbed in the filter accessory (Section 3.5). Sample collection from drone at the altitude from 50 to 400 m is seen in Supplemental Fig. S4. Aerosol particles were collected onto the filter attached to ITEX

unit in the drone. All the collected samples were wrapped in aluminum foil and placed into separate Minigrip bags which were stored in freezer (-20 °C) prior to analysis.

Portable BC and CPC devices were always active on measuring BC and total particle numbers during the fly of the drone. The detected BC and total particle numbers obtained with our portable devices were then compared with those obtained with reference devices at the SMEAR II Station (Section 3.7).

Table 1. Summary of target species, sampling and measurement techniques.

Target species	Sample phase	Sampler	Experiment(s)	Measurement technique
VOCs	Gas phase	ITEX + filter	Section 3.4	GC-MS
VOCs	Gas phase	SPME Arrow	Sec. 3.3; 3.4; and 3.6	GC-MS
VOCs	Particle phase	ITEX	Section 3.3 and 3.6	GC-MS
Carboxylic acids	Particle phase	Filter accessory	Section 3.5	HILIC-MS/MS
Black carbon	Particle phase	Portable AethLabs	Section 3.7	Real-time by Portable AethLabs
Total particle number	Particle phase	Portable CPC	Section 3.7	Real-time portable CPC

2.8. **Data Processing and statistical analysis**

Agilent ChemStation and Agilent Mass Hunter software were exploited for basic data processing, such as peak identification and integration. An Mzmine2 (version 2.53) software, consisting of an algorithm Automated Data Analysis Pipeline (ADAP-GC) was used for pre-processing untargeted mass spectrometric data for detection, deconvolution, and alignment of the chromatographic peaks in natural samples (Ruiz-Jimenez et al., 2019; Lan et al., 2021; Pusfitasari et al., 2022). NIST2020 (NIST MS Search v.2.3) mass spectral database was used to check and compare the mass spectra of the aligned peaks as well as their retention indices. The identified compounds should have a spectral match of >800 and ± 45 as the maximum difference between experimental and library Kováts retention indices.

Partial least squares regression (PLSR) equations were developed for the quantification and semi-quantification of the detected compounds in natural air samples (Kopperi et al., 2013; Lan et al., 2021; Pusfitasari et al., 2022). To develop different PLSR equations for the quantification/semiquantification of potentially identified compounds, six different concentration levels of 19 detected compounds, i.e. pyridine, sec-butylamine, 1-butanamine, butanenitrile, 2-propen-1-amine, diethylamine, dimethylformamide, hexylamine, trimethylamine, nonane, isobutanol, ethylacetate, methyl isobutyl ketone, hexanal, 2,3-

241 butanedione, benzaldehyde, acetophenone, p-cymene and ethyl benzene, were collected and analyzed under
242 optimal experimental conditions. Afterwards, the data was used for the development of the PLSR equation.

243 Total particle numbers measured by the reference instrument, an aerosol electrometer TSI 3772 at the altitude
244 of 4 m (ground level), were downloaded directly from the SmartSMEAR open-access database:
245 https://smear.avaa.csc.fi/ (Junninen et al., 2009).

246 The measured VOC values that were collected by ITEX sampling system, and BC as well as total particle
247 numbers at different altitudes were calculated to the same pressure level so that they could be compared to
248 literature values (Brasseur et al., 1999; Kivekäs et al., 2009; Rajesh and Ramachandran, 2018). In this study,
249 the reading values were corrected for ambient pressure and temperature as the following:

250 $$A = m_A \left[\frac{P_0 T}{P T_0}\right]^{-1} \quad (1)$$

251 where A is the corrected value, m_a is the measured raw concentration, P_0 is the standard atmospheric pressure
252 (101.3 kPa), T_0 is the standard temperature (293 K), P is the ambient atmospheric pressure, and T is the
253 ambient temperature. Supplemental Table S1 shows the data at ambient temperatures and pressures used in
254 this study, as well as the calculated correction factors at different altitudes. In the case of VOC concentrations
255 collected by SPME Arrows, no correction was applied since the equilibrium constant for current adsorbents
256 and compounds was not studied at various pressures and temperatures.

257 **3. Results and Discussion**

258 **3.1.Optimization of the sampling techniques using gas chromatography-mass spectrometry**

259 The choice of coating materials for SPME Arrow sampling systems was based on the good selectivity of
260 MCM-41 for nitrogen-containing compounds, suitability of DVB/PDMS for most of the VOCs present in the
261 air samples, and the capability of Carbon WR to collect volatile compounds, covers a wide range of polarity
262 and have a good reproducibility (Kim et al., 2020; Lan et al., 2019b; Ruiz-Jimenez et al., 2019). Whereas for
263 ITEX sampling system, the MCM-41-TP was chosen as a sorbent material since it has proved to have good
264 selectivity towards nitrogen-containing compounds, while TENAX-GR was selected due to its good
265 capability to collect different VOCs present in the air (Lan et al., 2019a; Pusfitasari et al., 2022).

266 The optimization containing equilibrium sampling time for SPME Arrow sampling systems, breakthrough
267 volume for MCM-41-TP-ITEX, desorption temperature and desorption time towards representative

compounds such as diethylamine, isobutylamine, triethylamine, trimethylamine, pyridine, p-cymene, 2-butanol and 2-butanone have been tested in our previous studies (Pusfitasari et al., 2022). Briefly, the average sampling time that is used before reaching equilibrium for both MCM-41-SPME Arrow and DVB/PDMS-SPME Arrow units is about 20 min. The cleaning and desorption temperature of 250 ºC for 10 min and 1 min, respectively, were selected to be optimal for the conditioning and analysis. The Carbon WR-SPME Arrow sampling system was also treated in the same way in terms of conditioning and desorption methods.

In our previous study, TENAX GR as the sorbent for ITEX's trap-accessory was able to adsorb mostly non-nitrogen containing compounds and only a small amount of nitrogen containing compounds (Pusfitasari et al., 2022). In the present study, universal TENAX-GR was used as ITEX sorbent material to collect air samples. Desorption and conditioning processes were optimized using a previously developed methodology and optimal conditions similar to MCM-41-TP-ITEX system with selective sorbent (section 2.4). The repeatability of TENAX-GR-ITEX sampler was also tested, with the RSD between 3.4 and 7.1 % (Supplemental Tables S2 and S3), whereas the reproducibility between different ITEX units caused also by ITEX manual packing was between 4 and 18 %.

The sampling systems used in this study needed to be stored for a certain period of time before analysis to accommodate the on-field situation. In our previous study, the sorbent in MCM-41-TP ITEX system could be stored at –20 ˚C up to 18 h without losing much of the model compounds, with the recoveries of around 80 % (Pusfitasari et al, 2021). For TENAX-GR sorbent, the recoveries of 98 % were obtained after storage at –20 ˚C for 24 h, but only 78 % when the sorbent was stored at room temperature for 24 h. In this study, the samples collected at the SMEAR II Station had to be analysed after storage of around 2 hours since the samplers were needed for the upcoming field measurements. Therefore, both MCM-41-TP- and TENAX-GR-ITEX systems were stored at room temperature only for a few hours before the analysis.

3.2. **Optimization of organic acid analysis using hydrophilic interaction liquid chromatography (HILIC)- tandem mass-spectrometry**

HILIC-ESI-MS/MS was employed for analysis of organic acid from filter samples. 18 different acids were successfully identified and five of them were quantified using the optimized method. For the 18 model acids, HILIC mobile phase with composition of ACN 80 % (solvent A) and 20 % of 0.005 % FA (solvent B) was chosen as the best eluent for acids separation (Supplemental Table S4). The second optimized parameter was drying gas temperature which is important parameter in the ESI technique to allow the eluent from the HILIC

column to evaporate as rapidly as possible in the ion source (Kruve, 2016). In this study, using the selected optimum eluent, i.e. ACN (80 %) and 0.005 % FA (20 %), with the flow rate of 0.25 mL min^{-1}, the drying gas temperature of 275 ºC was selected as the optimum temperature. Supplemental Table S5 shows the established multiple reaction monitoring (MRM) method parameters for each compound using all optimized parameters including the optimized voltages for other crucial parameters, namely fragmentor voltage, collision energy and cell acceleration voltage (CAV).

3.3.Application of air sampling system at the altitude from 50 to 400 m

In this study, the mesoporous silica-based materials, namely MCM-41 and MCM-41-TP, were used to selectively collect nitrogen-containing compounds (Lan et al., 2019b; Pusfitasari et al., 2022). Whereas the commercial universal materials, TENAX-GR and DVB/PDMS were also used to collect other than nitrogen-containing compounds.

MCM-41-TP-ITEX and TENAX-GR-ITEX sampling systems were used to collect atmospheric air samples containing both gas phase and aerosol particles, while the samples containing only gas-phase were collected by MCM-41-SPME Arrow and DVB/PDMS-SPME Arrow systems. The concentrations in aerosol particles were obtained via the subtraction of these results, i.e. MCM-41-TP-ITEX subtracted with MCM-41-SPME Arrow, and TENAX-GR-ITEX subtracted with the DVB/PDMS-SPME Arrow.

Altogether, up to 40 VOCs were detected in gas phase and 48 were in particle phase samples. VOCs with various functional groups such as nitrogen-containing compounds, alcohols, ketones, aldehydes, small organic acids, and hydrocarbons were detected both by selective MCM-41 coated SPME Arrow and MCM-41-TP-ITEX sampling systems and by universal sorbent materials TENAX-GR-ITEX and DVB/PDMS coated SPME Arrow systems. However, because in our previous study (Lan et al., 2019b; Pusfitasari et al., 2022), the MCM-41-SPME Arrow and MCM-41-TP-ITEX samplers gave sensitive and reliable results in collecting selectively nitrogen-compounds, only the results obtained by MCM-41-SPME Arrow and MCM-41-TP-ITEX samplers are shown for nitrogen-containing compounds in this section. While data for other VOCs were collected using ITEX with universal sorbent materials TENAX-GR and using DVB/PDMS coated SPME Arrow.

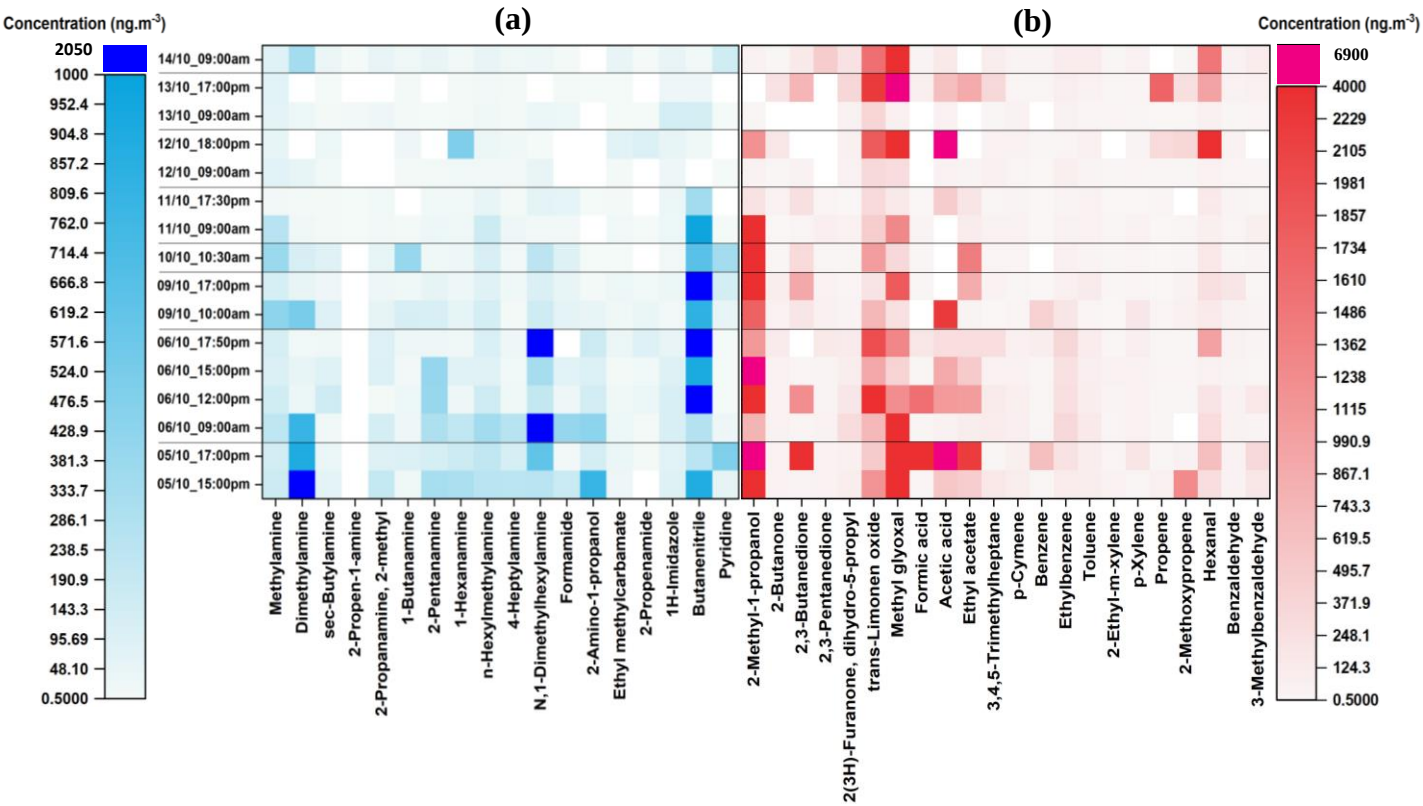


Figure 2. Concentrations of **(a)** nitrogen-containing compounds and **(b)** other VOCs in the gas-phase at the SMEAR II Station, Hyytiälä at the mixed altitude between 50 and 400 m. **(a)** Nitrogen-containing compounds were collected using MCM-41-SPME Arrow system with selective sorbent, while **(b)** other VOCs were collected using DVB/PDMS-SPME Arrow system with universal sorbent. White color = not detected.

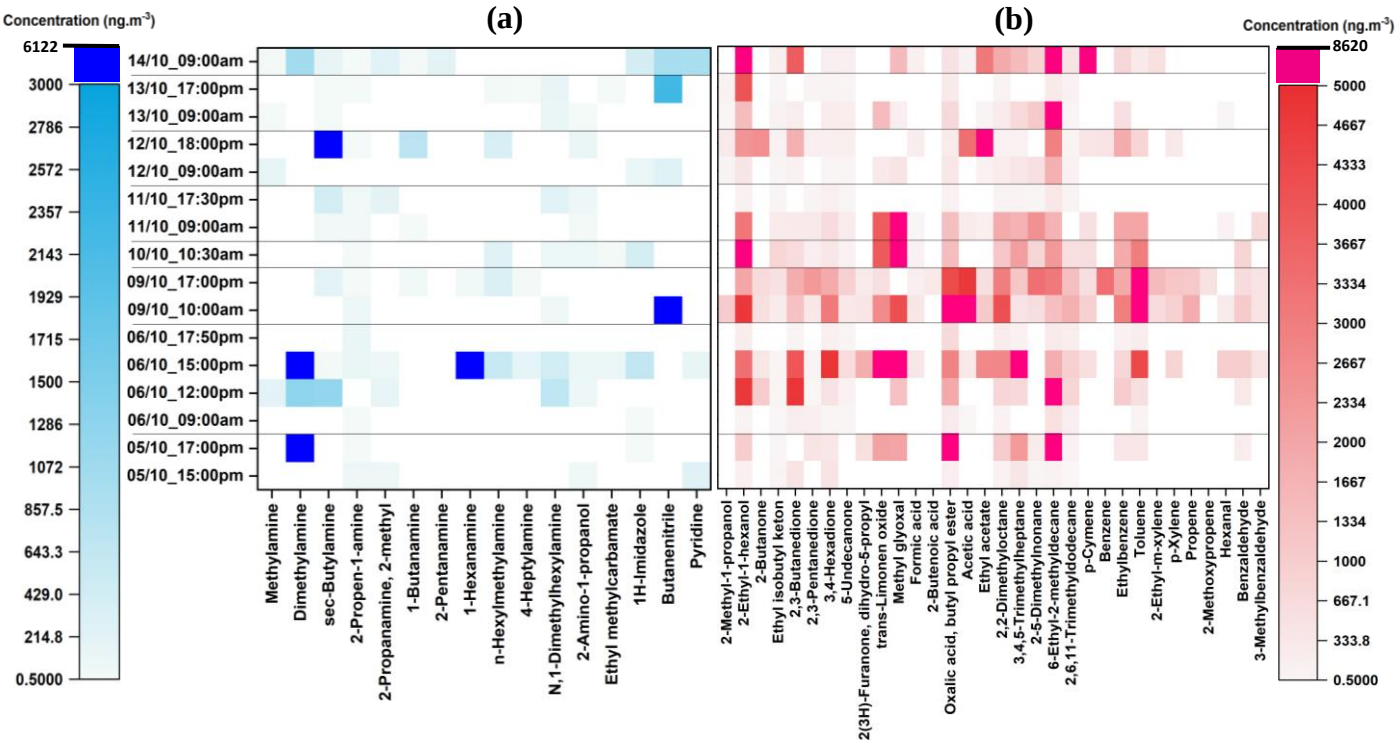


Figure 3. Concentrations of **(a)** nitrogen-containing compounds and **(b)** other VOCs in the particle phase at SMEAR II Station, Hyytiälä at the mixed altitude between 50 and 400 m. Samples were collected using MCM-41-TP-ITEX system with selective sorbent **(a)** and TENAX-GR-ITEX systems with universal sorbent **(b)**. White color = not detected.

As can be seen from Fig. 2, eleven aliphatic amines (methylamine, dimethylamine, sec-butylamine; 2-propen-1-amine; 2-methyl-2propanamine; 1-butanamine, 2-pentanamine, 1-hexanamine, n-hexylmethylamine, 4-heptylamine, N,1-dimethylhexylamine) and seven other nitrogen-containing compounds (formamide, 2-amino-1-propanol, ethylmethylcarbamate, 2-propenamide, 1H-imidazole, butanenitrile, and pyridine) were detected, quantified and semi quantified in gas phase samples with the concentrations up to 2005 ng m^{-3}. While in the particle phase (Fig. 3), the total of 16 nitrogen-containing compounds was detected with the concentrations up to 6122 ng m^{-3}. These results are comparable to our previous study in which the concentrations of nitrogen-containing compounds were up to 2930 ng m^{-3} and 5480 ng m^{-3} in gas phase and particle phase, respectively (Pusfitasari et al., 2022). However, the samples were collected then at the altitude from 50 to 150 m (Pusfitasari et al., 2022).

Dimethylamine, that can be produced by animal husbandry, cattle, landfill, sewage, and also industry (Ge et al., 2011), was detected in both gas and particle phase during afternoon with the concentrations up to 1004

ng m^{-3} for gas phase, and up to 5909 ng m^{-3} for the particle phase (Fig. 2a and Fig. 3a). Studies have indicated that organic amines, including DMA, can be present to large extent in the particles e.g. by transferring from gas phase to particles (Chen et al., 2022; Zhao et al., 2007; Yu et al., 2017). DMA is one of the most common and abundant amines found in the atmosphere, and particulate DMA concentrations can increase due to enhanced BVOC emissions and due to aerosol-phase water that increase their partition to the condensed phases (Ge et al., 2011; Youn et al., 2015; Chen et al., 2017).

Other amines that were detected at high concentrations were methylamine, pentanamine, hexanamine, hexylmethylamine, and dimethylhexylamine with the concentrations up to 432, 395, 493, 340, and 1393 ng m^{-3}, respectively (Fig. 2a). For the particles, sec-butylamine was detected with the concentrations up to 4090 ng m^{-3}, hexanamine up to 4316 ng m^{-3} and dimethylhexylamine up to 686 ng m^{-3} (Fig. 3a).

For nitrogen-containing compounds other than amine, butanenitrile was detected as the highest concentrations up to 2005 ng m^{-3} in gas and 6122 ng m^{-3} in particle phases. 2-Amino-1-propanol, pyridine, and 1-H-imidazole were present in gas phase as the second, third and fourth highest concentrations up to 790, 492, and 136 ng m^{-3}, respectively. While in the particle phase, their concentrations were up to 129, 958, and 646 ng m^{-3}, respectively. The concentrations of all detected nitrogen-containing compounds at mixed altitudes can be seen in Supplemental Table S7.

For other VOCs, 22 compounds in gas phase (Fig. 2b) and 32 in particle phase (Fig. 3b), containing alcohols, aldehydes, ketones, small organic acids and hydrocarbons were detected and quantified or semi quantified with the concentrations up to 6898 ng m^{-3} in the gas phase and 8613 ng m^{-3} in the particle phase. In the gas phase, 2-methyl-1-propanol; 2,3-butanedione; trans-limonene oxide, methylglyoxal, acetic acid, ethyl acetate, and hexanal were discovered almost all the time during the samplings with the concentration up to 4209, 2436, 2210, 4695, 6898, 2198 and 3984 ng m^{-3}, respectively (Fig. 2b). While in the particle phase, almost all detected compounds were present in high concentrations such as 2-ethyl-1-hexanol (4114 ng m^{-3}); 2,3-butanedione (4865 ng m^{-3}), trans-limonene oxide (6886 ng m^{-3}), methylglyoxal (8613 ng m^{-3}), aliphatic hydrocarbons (7091 ng m^{-3}), ethyl benzene (3042 ng m^{-3}) and toluene (7715 ng m^{-3}) , (Fig. 3b). Supplemental Table S8 gives at mixed altitudes (50 to 400 m) the concentrations for all detected VOCs that do not belong to nitrogen-containing compounds.

In the atmosphere, 2,3-Butanedione is naturally occurring in food products such as butter and beers (Boylstein et al., 2006), while trans-limonene oxide is detected possibly due to the partial oxidation of monoterpene limonene's olefinic bonds (Hoeben et al., 2012; Karlberg et al., 1992). Methylglyoxal, an important precursor

of SOA, is produced in the atmosphere by the oxidation of hydrocarbons, such as isoprene, acetylene, toluene, and xylenes (Zhang et al., 2016; Fu et al., 2013; Olsen et al., 2007). Other detected compounds, e.g. acetic acid and ethyl acetate can be released from different sources such as biomass burning and vegetation (Rosado-Reyes and Francisco, 2006; Khare et al., 1999).

The diurnal pattern in both gas and particle-phases was also observed. As can be seen from Fig. 2 in the gas phase, aliphatic amines that are mostly emitted by biogenic sources were present in lower concentrations in the evening (started at 17:00 pm) compared to daytime, whereas some amines, namely hexanamine and dimethylhexylamine, had slightly higher concentrations in the evening. These results agree well with our previous study in which most of the amines had a diurnal variation with a daytime maximum due to their dependency on temperature for their emission, indicating the contribution to biogenic sources (Pusfitasari et al., 2022). High concentrations of some amines in the evenings could be caused by the weak atmospheric mixing at night resulting in decreased reactions with atmospheric acids (Hemmilä et al., 2018). In contrast, VOCs that were emitted from other sources had higher concentrations mostly in the afternoons, except for non-nitrogenated compounds with high concentrations also in the mornings on 11 October 2021. The anthropogenic sources that might affect this result, were probably carried by the wind from other places and were mixed in the atmosphere since the samples were collected at high altitudes (up to 400 m). In the particle phase, there was no clear pattern seen since our samples were mostly collected only in the mornings and late afternoons. However, in our previous study we found that VOCs had high concentrations in mornings and evenings since temperature dependency affects the deposition of amines in the colder evenings, and then they partition back to the atmosphere in the higher temperature mornings (Pusfitasari et al., 2022). In this present study we can also see from Fig. 3 high concentrations both in the mornings and late afternoons, but surprisingly also at noon (on 6 October).

The correlation among all the VOCs in both gas and particle phases was also studied. R-value close to one and P-value <0.05 mean that there is correlation between variables. As can be seen from Supplemental Fig. S5, only a few compounds in gas phase correlate with those detected in the particle phase, such as particulate benzaldehyde that correlated with alcohol vapors (i.e. gas-phase of 2-methyl-1-propanol and 2-ethyl-1-hexanol) and some amines (i.e. methylamine, sec-butylamine, 2-pentanamine, and n-hexylmethylamine). These correlations can be explained by the studies conducted by Perez et al (2017) who was investigating the implication of aldehyde – amines to the aerosol growth by providing low-energy neutral pathways for the formation of larger and less volatile compounds (Perez et al., 2017).

In addition, we can also see that some nitrogen-containing compounds correlated with aliphatic hydrocarbons, aliphatic carbonyl, and aliphatic alcohols in the gas phase, indicating that they might be emitted from the same sources. This finding is supported by the study conducted by Isidorov *et al* (2021). Although their group could not detect selectively nitrogen-containing compounds because they used universal sorbent material for the collection of air sample (i.e. DVB/CAR/PDMS-SPME), they could detect all other VOCs compounds at the same time from the boreal forest (Isidorov et al., 2022).

3.4. Evaluation of ITEX filter accessories

In our previous study, it was proved that a small filter can be used to trap particles allowing only gas phase enter the ITEX sampler (Pusfitasari et al., 2022; Ruiz-Jimenez et al., 2019). The experiments were properly designed to check and compare the results achieved for gas phase compounds using a passive SPME Arrow and an active ITEX + filter sampling systems. In the present study, the samples were collected from 11 to 14 October 2021 and TENAX-GR-ITEX was exploited with the filter accessory. The altitudes for these experiments were 50-400 m (Supplemental Fig. S1). As can be seen in Supplemental Fig. S6, aliphatic amines were the major nitrogen-containing compounds detected both in the gas and particle phases. For VOCs without any nitrogen compounds, following the results in the previous section (i.e. section 3.3.), alcohols, ketones, aldehydes, organic acids and some hydrocarbons were detected, quantified and semiquantified with the concentrations shown in Supplemental Fig. S6. The results of the gas-phase sampled by ITEX system with filter accessory were comparable with the gas phase results obtained by the SMPE Arrow sampling system.

~~In addition to the comparison of gas phase collected by ITEX (+ filter accessory) and SPME Arrow systems, the recoveries of gas phase obtained by the first sampling system were also evaluated.~~ In addition to the comparison of gas phase collected by ITEX furnished with filter accessory and by SPME Arrow system, the compound recoveries of gas phase obtained by the first sampling system ITEX furnished with filter were also evaluated. The recoveries of non-polar compounds, such as alkanes, were only <50 % (Supplemental Table S9). The more polar compounds, such as alcohols, acids, and nitrogen-containing compounds, were mostly detected at higher recoveries from 50 % up to 99 %. Most probably non-polar compounds of the gas phase were partly adsorbed to the ITEX filter accessory that was made from PTFE (Parshintsev et al., 2011). PTFE has a non-polar structure due to the distribution of the fluorine atom around the carbon polymer backbone which balances the electronegative and electropositive charges (Parsons et al., 1992). Hence, our study proved that ITEX with PTFE filter does not only trap aerosol particles but is also excellent for the collection of polar compounds, such as nitrogen-containing compounds, of gas phase. Nevertheless, since nitrogen-

containing compounds are very water soluble, the humidity level in the air will most likely affect the distribution of polar compounds between the filter and ITEX adsorbent, e.g. water condensing to the filter at high humidity.

3.5. Analysis of aerosol particles collected by ITEX with PTFE filter using liquid chromatography tandem mass spectrometry

Filter collecting aerosol particles in ITEX was extracted and analyzed separately by using HILIC-MS/MS to quantify carboxylic and dicarboxylic acids since most organic acids cannot be analyzed by GC without derivatization, except small organic acids such as formic acid and acetic acid. The organic acids have capability to significantly enhance the hygroscopicity of aerosol particles and contribute to the acidity of precipitation and cloud water.

As can be seen in Table 2, five main acids, succinic acid, benzoic acid, phthalic acid, glutaric acid, and adipic acid, were identified and quantified. Succinic acid was observed almost in every sample and its higher prevalence could possibly be explained by the fact that it can be formed from common biogenic and anthropogenic precursors such as isoprene and toluene (Sato et al., 2021). The aromatic acids such as benzoic acid and phthalic acid were also detected in the samples. The concentrations of benzoic acid (up to 1.4 μg m^{-3}) were higher than those of phthalic acid (up to 0.77 μg m^{-3}). Observation of these acids is relevant as their aromatic hydrocarbon precursors are common in the atmosphere. In addition, phthalic acid has also been detected in the summer 2012 samples, but then no benzoic acid was detected in the gas phase or particulate phase (Kristensen et al., 2016).

Table 2. Concentrations of acids collected from the ITEX filters at the altitudes of 50-400 m.

Sampling time	Succinic acid (ng m^{-3})	Benzoic acid (ng m^{-3})	Phthalic acid (ng m^{-3})	Glutaric acid (ng m^{-3})	Adipic acid (ng m^{-3})
11.10.2021	1416	1416	657	1619	10926
12.10.2021	435-789	1416	769	n.d.	n.d.
13.10.2021	496-4654	n.d.	n.d.	n.d.	n.d.
14.10.2021	n.d.	n.d.	n.d.	1720	6374

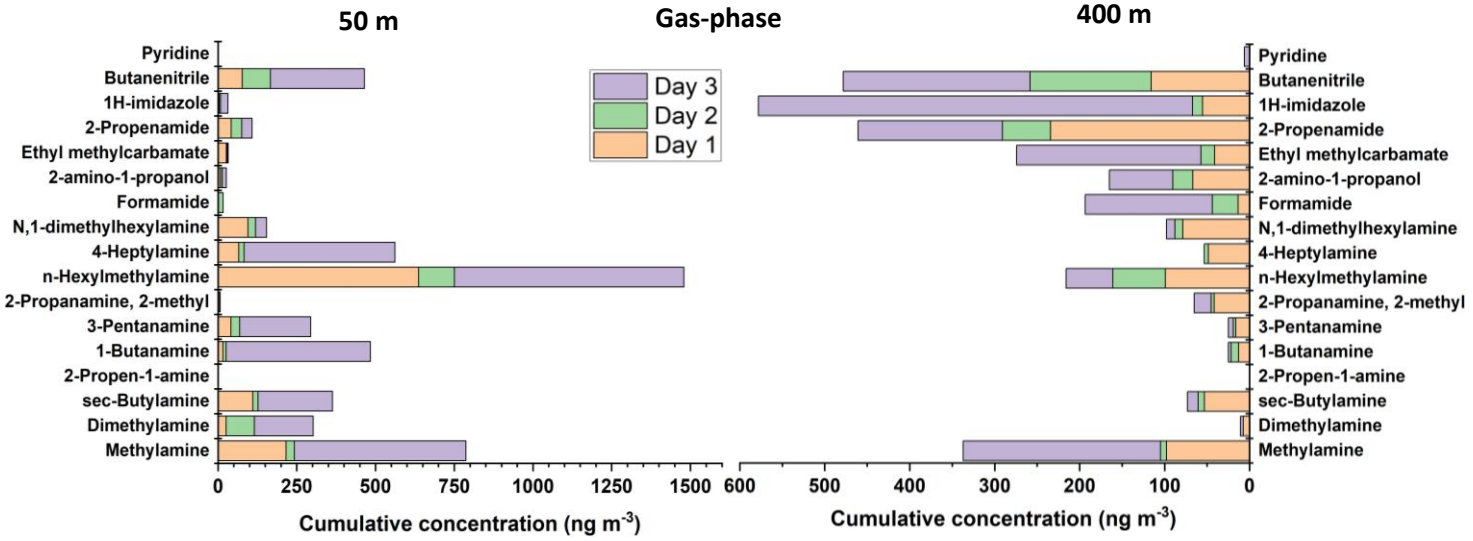
*n.d. = not detected

Glutaric and adipic acids were also determined from samples taken on the 11th and 14th of October. Glutaric acid and adipic acid have been commonly detected in atmospheric aerosols and cloud droplets (Wen et al., 2021). Other dicarboxylic acids, such as glycolic acid and cis-pinonic acid were detected in only one sample

in which their LODs were exceeded (Supplemental Table S10). The possible reason for the low concentration of glycolic acid might be that it can be formed as an oxidation product of biogenic isoprene (Liu et al., 2012).

3.6.Comparison of nitrogen-containing compounds and other VOCs at the altitudes of 50 m and 400 m

The aim of this study was to compare the composition of VOCs at the altitudes of 50 m and 400 m, separately. Carbon WR-SPME Arrow unit with universal sorbent was used to collect a wide range of VOCs in the gas phase. MCM-41-TP-ITEX and TENAX-GR-ITEX sampling systems were employed to collect gas and particle phases.



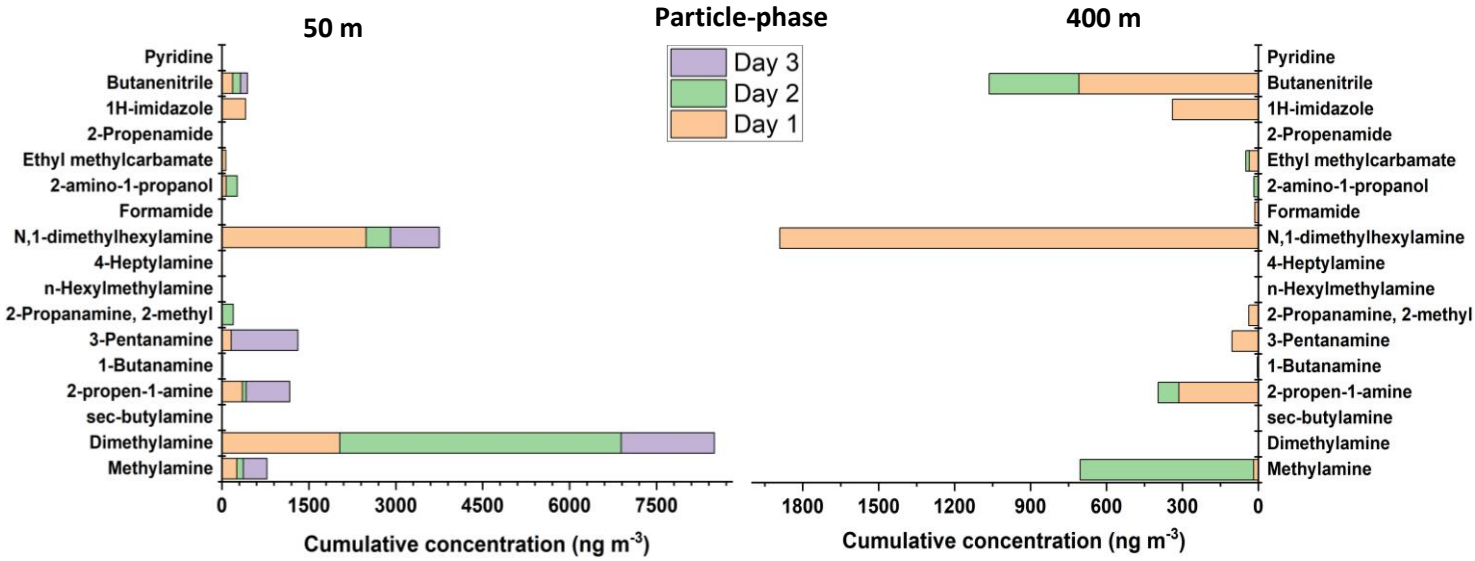
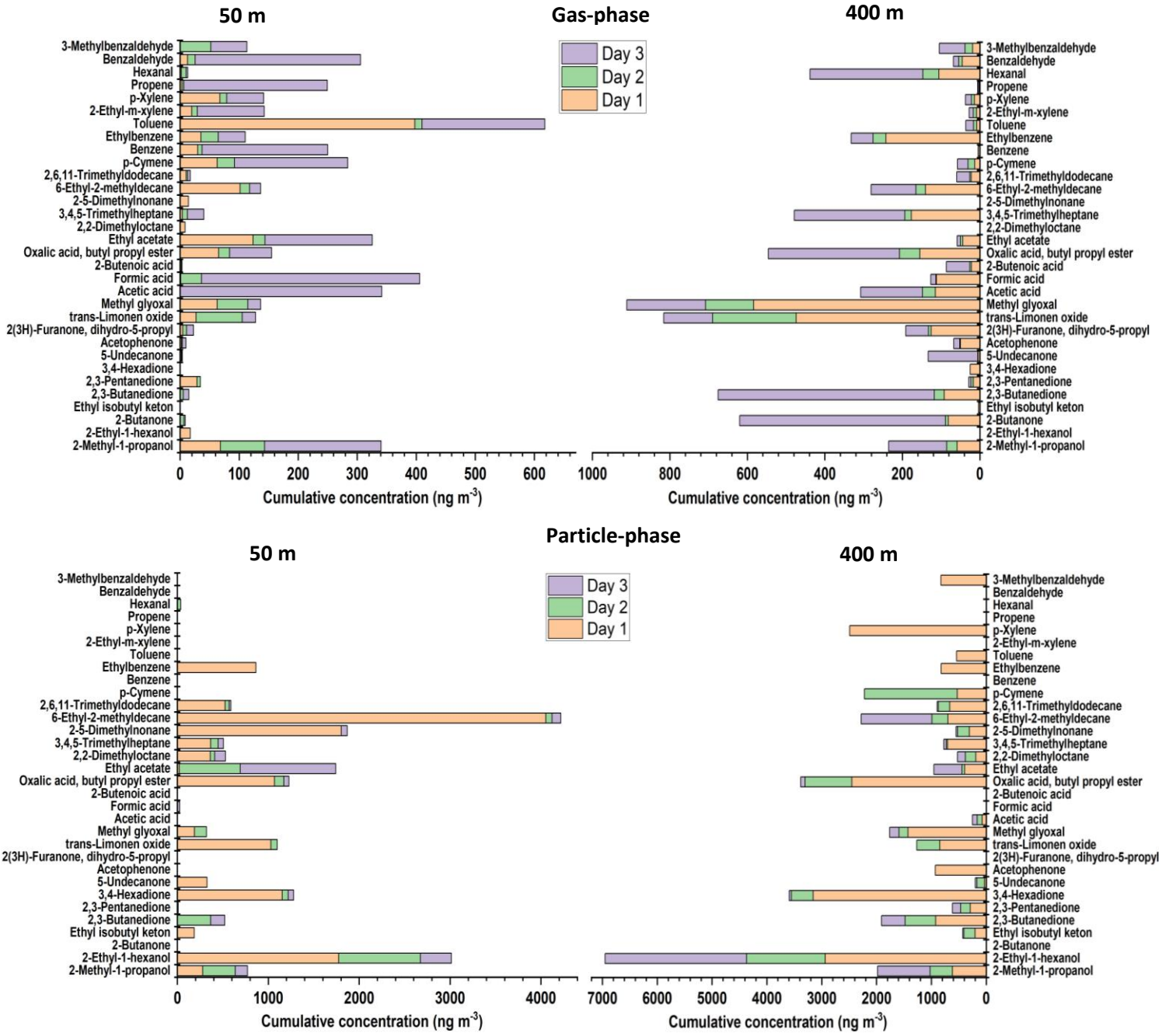


Figure 4. Concentrations of nitrogen-containing compounds in the gas-phase and in particle-phase at SMEAR II Station at altitudes 50 and 400 m for three days (8 to 10 October 2021). For the gas-phase samples were collected using Carbon WR-SPME Arrow sampling system, and the particle-phase samples were collected by MCM-41-TP-ITEX system. The concentrations of aerosol particle compounds were obtained via subtraction the results obtained by MCM-41-TP-ITEX from those obtained by Carbon WR-SPME Arrow with universal sorbent.

As can be seen from Fig. 4, the concentrations of amines that were emitted by biogenic sources, such as methylamine, dimethylamine, sec-butylamine, butanamine, pentanamine, hexylmethylamine, and heptylamine, were mostly found at higher concentrations at the lower altitude (50 m). The concentrations were decreased at higher altitude 400 m most probably due to the dilution (since the sources are on the ground) and reaction with hydroxyl radical (Kieloaho, 2017).

For nitrogen containing compounds, other than amines, imidazole was one of the compounds detected by our system. There have been a number of laboratory studies where imidazole has been reported to be the major product of glyoxal reaction with ammonium ions or primary amines on secondary organic aerosol. In addition, imidazoles can become a secondary product of the reaction of dicarbonyls with nitrogen containing compounds, therefore they might have potential to act as photosensitizers triggering secondary organic aerosol growth and are forming constituents of light absorbing brown carbon (De Haan et al., 2011; Dou et al., 2015; Teich et al., 2020). Imidazoles were detected mostly in the particle phase with concentrations up to 422 ng m^{-3} at 50 m and 338 ng m^{-3} at 400 m. Slightly lower concentrations were discovered in the gas phase with the values up to 58 ng m^{-3} at the altitudes of 50 m, and 510 ng m^{-3} at the altitude of 400 m.

Other nitrogen-containing gas phase compounds detected, such as formamide, 2-amino-1-propanol, ethylmethylcarbamate, and propenamide showed also the same pattern with higher concentrations at 400 m than at 50 m. These compounds were most probably transported by the wind from other areas and emitted by various sources, such as biomass burning, peatland, industries, and other anthropogenic sources (Pusfitasari et al., 2022).



499 **Figure 5.** Concentrations of non-nitrogenated VOC compounds in the gas-phase and in particle-phase at
500 SMEAR II Station at altitudes 50 and 400 m for three days (8 to 10 October 2022). The gas-phase samples
501 were collected using Carbon WR-SPME Arrow system, and particle-phase samples using TENAX-GR-ITEX
502 sampling systems. The concentrations of aerosol particle compounds were obtained via subtraction the results
503 obtained by TENAX-GR-ITEX from those obtained by Carbon WR-SPME Arrow with universal sorbent.

As can be seen from Fig. 5 gas-phase VOC compounds without nitrogen, such as trans-limonene oxide, methylglyoxal, hexanal and ketones have higher concentrations at the altitude of 400 m compared to 50 m. Whereas some acids, such as acetic acid and formic acid, ethyl acetate, and BTX (benzene, toluene, xylene) were mostly discovered at the altitude of 50 m. In the case of alcohols, they had comparable concentrations at both 50 and 400 m. In the particle phase, most of the compounds had higher concentrations at 400 m than at 50 m, except for some hydrocarbons (such as 2,5-dimethylnonane and 6-ethyl-2-methyldecane) that had high concentrations at 50 m.

Alcohols are a prevalent class of VOCs in the atmosphere and can be emitted by biogenic sources such as rain forest, and also from anthropogenic sources such as alcohol-gasoline blended fuel and industries (Nguyen et al., 2001; McGillen et al., 2017). Therefore, it is no wonder that in this study alcohol was found almost in all altitudes. The alcohol emission is becoming concern since it can react with Criegee intermediates (product of biogenic alkenes oxidized by ozone) to produce α-alkoxyalkyl hydroperoxides (AAAHs) that can lead to the formation of secondary organic aerosols (Sahli, 1992; Bonn et al., 2004; McGillen et al., 2017).

In the gas phase samples, benzene, toluene, and p-xylene (BTX) were found mostly at the altitude of 50 m with the concentrations up to 219, 410, and 70 ng m^{-3}, respectively. Since BTX can be emitted from the gasoline (major fuel of vehicles) and the samples were collected close to the parking area, the higher concentrations were found at lower altitude 50 m. This finding is comparable with the study conducted by Chen et al (2018) who measured the BTX concentrations between 100 and 300 ng m^{-3} from forest canopy at the altitude between 20 and 26 m ~~m $^{-3}$~~ (Chen et al., 2018; Yassaa et al., 2006). Toluene and p-xylene were also detected in the particle phase as VOCs may be adsorbed onto the surface of the particles (Dehghani et al., 2018; Kamens et al., 2011). The higher concentrations were detected at the altitude of 400 m with the concentrations of up to 539 ng m^{-3} and 2475 ng m^{-3} for toluene and p-xylene, respectively. BTX play an important role in the atmosphere since they have been recognized as important photochemical precursors for the secondary organic aerosol (Correa et al., 2012; Ng et al., 2007).

Aldehydes in the atmosphere are also of concern because of their heterogeneous reaction with acids affecting the particle growth (Jang and Kamens, 2001; Altshuller, 1993). In our study, some aldehydes, such as methylglyoxal, hexanal and benzaldehyde, were found both in the gas and particle phase at the altitude of 400 m in higher concentrations than at the altitude of 50 m. At the altitude of 400 m, methylglyoxal was the most abundant aldehyde with the concentrations up to 580 ng m^{-3} in the gas phase, and 1418 ng m^{-3} in the particle phase. Ketones in aerosol particles have been associated with burning and non-burning forest, and it

represented up to 27 % of the current organic aerosol mass concentration (OM) (Takahama et al., 2011). Ketones were also found in this study at higher concentrations at high altitude 400 m in both gas phase and particle phase.

The last group of chemicals that was detected by our collection systems was small organic acids, and from these especially formic acid and acetic acid. Organic acids have an important role as chemical constituent in troposphere and they contribute with a large fraction (25 %) to the nonmethane hydrocarbons in the atmosphere. The organic acids contribute to the acidity of precipitation and cloud water (Khare et al., 1999). Acetic acid was found in both gas and particle phases at the altitudes of 50 and 400 m. However, the amount of both formic acid and acetic acid found in the gas phase was higher than that in the particle phase. These acids can originate from various sources such as vehicular emissions, ants, plants, soil, and biomass burning (Zhang et al., 2022).

3.7. Evaluation of total particle numbers and black carbon at high altitudes. Portable CPC and BC devices carried by aerial drone

The particle number concentration and BC concentration were measured by using portable CPC and BC measurement devices carried by the drone. The BC concentration was measured at 880 nm wavelength (near IR), as at this wavelength BC has strong absorption and least interferences by other organic molecules (Dumka et al., 2010). The results were compared to those measured by the reference instruments at the SMEAR II Station. The correction factors to the same pressure level as described in section 2.8 were calculated with the values between 0.994 and 1.035 (Supplemental Table S1). Supplemental Figure S7 for CPC proves a correlation between the results obtained by our portable CPC and reference instrument, with direct linear close to 1 (R^2 of 0.9564). Oppositely, linear correlation for BC was only 0.2492, indicating that there was no correlation between the reference instruments and our BC meter in the drone.

Our portable BC monitor in the drone gave higher concentration values than the reference one, located at 4 m. The reasons for the differences could be caused by amplification factor that raised due to multiple scattering in quartz fiber matrix of the tape of the Aethalometer. The deposition of scattering material along with BC to the filter tape produced the "shadowing effect" causing the BC meter to show higher concentration values (Weingartner et al., 2003; Dumka et al., 2010). Alternatively, the differences can be explained by different measurement altitudes between the reference instrument (measured at 4 m) and BC monitor in the drone (up to 400 m). At lower altitude, living activities such as heating sauna and fuel burning from cars nearby the area might contribute to the results, while at higher altitudes BC long distance transport contributes

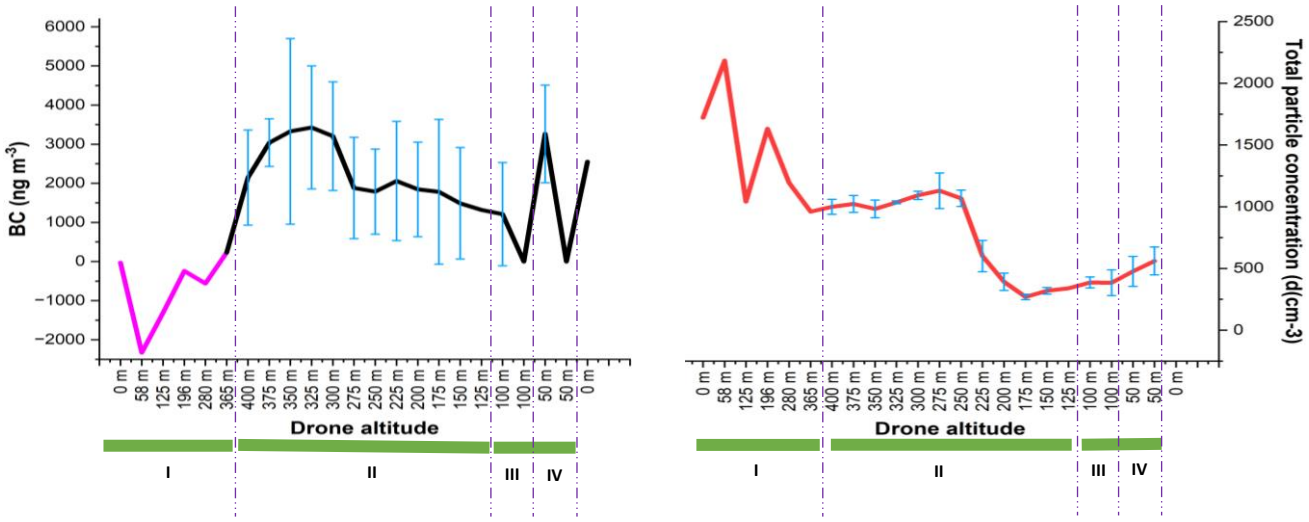
to the results as well (Meena et al., 2021). The atmospheric boundary layer height (ABLH) also plays an important role to govern concentration of BC at high altitudes since it can affect pollutant aggregation, transmission, wet deposition, and dry sedimentation (Meena et al., 2021). The boundary layer (BL) is the lowest part of troposphere and connects the ground and the free atmosphere. The average boundary layer height at Hyytiälä SMEAR II Station in autumn (October) was around 500 m (Sinclair et al., 2022), explaining why we found higher BC concentration at high altitudes. For comparison, Table 3 shows the BC mass concentrations measured at high altitudes in different areas.

Table 3. Average BC concentrations observed at different locations.

Location	Altitude	Environment	Average BC concentration (ng m^{-3})	Reference
Hyytiälä, Finland	100 m	Boreal forest	2278±1188	This study
Hyytiälä, Finland	200 m	Boreal forest	2500±1497	This study
Hyytiälä, Finland	300 m	Boreal forest	3564±1648	This study
Hyytiälä, Finland	400 m	Boreal forest	3909±729	This study
Hyytiälä, Finland	4 m	Boreal forest	320 – 1291 ± 337*	(Hyvärinen et al., 2011)
Mahabaleswar, India	1378 m	Rural	2600 ± 260	(Meena et al., 2021)
Mountain Huang, China	1840 m	Rural	1663±919	(Pan et al., 2011)
Port Blair, India	73 m	Rural	2446±66	(Moorthy and Babu, 2006)
Sinhagad, India	1300 m	Rural	1500	(Safai et al., 2007)

*****320 ng m^{-3} was the annual average, while 1291 ng m^{-3} was the concentration average measured during pollution event in Autumn

Autumn average of BC pollution in Hyytiälä according to Hyvärinen *et al*. 2011 was about 1291 ng m^{-3}, while Hienola *et al* (2013) reported the October average was 550 ng m^{-3} (Hyvärinen et al., 2011; Hienola et al., 2013). However, those studies were conducted using reference instrument at low altitude, i.e. 4 meters above the ground.



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578 **Figure 6.** Evaluation of drone's vertical and horizontal movements. I = Drone is moving up with the speed
579 of 2.5 ms^{-1}. II= Drone is descending with the speed of 1.25 ms^{-1} to each altitude before staying for 30 s. III
580 and IV = Horizontal movement to 100 m far with the speed of 5 ms^{-1}.

581 The drone stability was evaluated during the vertical and horizontal movements (drone movement schematic
582 is showed in Supplemental Fig. S4). Figure 6 shows that the BC concentration and total particle numbers
583 were affected by the drone movements. Rapid ascending (area number I) affected both BC and CPC. BC
584 measurements showed negative values when the drone started warming up, take off, and then quickly moved
585 vertically with the speed of 2.5 ms^{-1}. These readings could be due to the temperature change on the BC sensor
586 when the drone ready to take off and drone fast ascending (Pan et al., 2011; Elomaa, 2022). Portable CPC
587 device gave also fluctuating data. Both BC device and CPC started to stabilize when approaching altitude of
588 365 m.

589 At the beginning of drone vertical movement at the altitude of 400 m, portable CPC gave more stable results
590 when the speed was decreased and when it was allowed to stabilize for 30 seconds (as can be seen in area
591 number II), resulting in smooth changes in the total particle numbers and some deviations at each altitude.
592 However, BC concentration varied also with high standard deviations at high altitude without any specific
593 movement, indicating that the drone movement influenced the portable BC device. Pan *et al* (2011) have
594 suggested that a large variation in the BC measurements could be caused by several factors such as boundary
595 layer stratification and turbulence. In addition, BC sensor was also very sensitive to change in temperature.
596 They observed that BC concentration could change quickly only after a short period of sunshine. Based on

the standard deviations' horizontal movements (area numbers III and IV), affected much less portable CPC, compared to the portable BC.

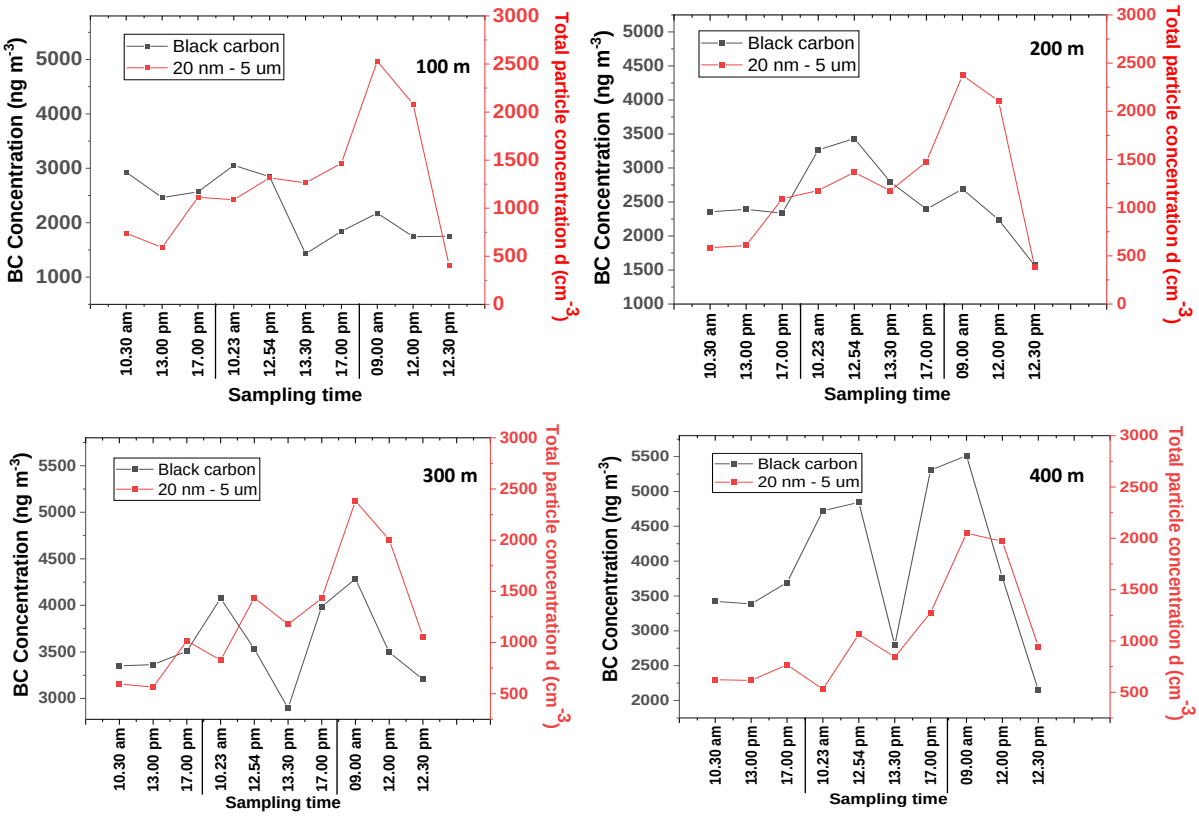

Figure 7. Time series evaluation of CPC and black carbon at the heights of 100, 200, 300, and 400 m. Sampling was conducted on October 9 (Day 1), 10 (Day 2), and 11 (Day 3), 2021. The values and point averages are shown in Supplemental Table S11.

It can be seen from the results of Fig. 7 for three days measurements that BC and CPC had similar pattern at all altitudes (100, 200, 300 and 400 m). The daily means of total particle numbers are found from Supplemental Table S12. Although the concentrations at the altitude of 400 m seem to be slightly lower than those detected at lower altitudes, the patterns of total particle number are similar at every altitude (Fig. 7), most possible due to the limited anthropogenic activities near the sampling site. The potential mixing and the particle formation in the atmosphere most likely influenced the total particle number detected. In addition, particulates' long-range transport from different areas could also affect the total particle concentration in the air (Casquero-Vera et al., 2020).

Figure 7 also demonstrates that diurnal pattern was different, revealing that the particle concentrations at different times of the day were influenced by different sources compared to BC. Almost at all altitudes, the diurnal variation for day 1 and day 2 included a late afternoon peak at 17:00. The particle concentrations increased significantly on the day 3, especially during the first and second samplings before the change to lower concentrations. The samplings for the first two days were carried out during the weekend without many activities that produce VOCs, opposite to Monday morning, when the normal working activities close to sampling area were going-on.

In contrast to the pattern of total particle numbers, the daily average of BC concentration during the measurement time period was increased at higher altitudes (Supplemental Table S12), indicating that BC pollutant was distributed from different areas. These trends agree well with the earlier studies (Tripathi et al., 2007). Figure 7 shows that BC diurnal pattern was similar with that of total particle numbers, except on day 2 when BC concentration decreased significantly at 13.30, excluding the altitude of 200 m. However, BC concentration increased again at 17.00 most likely due to e.g. sauna heating and air mixing following long-range transport from different areas.

During the measurement time, BC at high altitudes 400 m and total particle numbers at all altitudes (100 – 400 m) showed diurnal cycle with peak observed on Monday morning at 09:00 am, possible due to morning traffic, and/or to wind-driven pollution transport as suggested by previous studies (Bonasoni et al., 2010; Sandeep et al., 2022). The high BC concentration at high altitude, especially at 400 m, was mostly caused by long-range transport and the atmospheric boundary layer height as discussed earlier, and BC and also other particles contributed to the total particle numbers.

4. Conclusions

An aerial drone carrying the reliable and versatile miniaturized air sampling systems SPME Arrow and ITEX and portable BC and CPC devices was successfully used for the collection of air samples. Up to 48 VOCs were detected in gas and particle phase samples, and their distribution at the altitude from 50 to 400 m was studied. Some differences between VOC compositions at the altitude 50 and 400 m could be explained by the different sources of the VOC emissions. The compounds that most probably originate from the same source had a linear correlation, as well as the compounds that were present both in gas and particle phase samples. The capability of ITEX sampler, furnished with filter accessory for the collection of gas phase samples, was evaluated by comparing it with SPME Arrow sampling resulting in high agreement especially for polar compounds with recoveries up to 99 %. In contrast, non-polar compounds gave low recoveries due

to the *like dissolve like* rule meaning that non-polar compounds might be adsorbed to the non-polar PTFE filter of the ITEX sampling system.

The portable CPC gave comparable results with those obtained by the conventional reference CPC instruments at the SMEAR II Station, opposite to the portable BC device that was affected by drone's vertical and horizontal movements. The total particle number and BC gave similar diurnal pattern, indicating that they were correlated. The pattern was observed during the weekend. The highest concentrations were found during times with human activities. The distribution was also similar to VOCs that were produced by anthropogenic sources and found in high altitude samples, since the wind most probably carried the VOCs from other sites. For spatial distribution pattern, BC concentrations were increased at higher altitudes due to long-range transport and the atmospheric boundary layer height. The total particle numbers, affected by the similar factors, varied more depending on the sources. This can be explained by the different VOCs that contributed to the particle formations, and the particle sizes measured by the portable CPC and BC monitors.

Overall, our study work described a drone equipped with miniaturized air sampling techniques, SPME Arrow and ITEX together with portable BC and CPC devices were for the collection of atmospheric VOCs and for the measurement of BC and total number of particles at high altitudes. To further improve the reliability of the results in the future, a portable BC monitor that includes a better electronic model and the possibility to adjust the device position in the drone are needed.

Author contributions. EDP, JR-J, JH, KH, MJ, TP and M-LR designed the experiments. EDP, AT, MS, JR-J carried out the experiments. EDP performed data interpretation and visualization. JR-J performed the statistical analysis. YW, JH, JK and KL were responsible for CPC and BC hardware, software and reference data. EDP, JR-J, KH, TP and M-LR prepared the manuscript with contributions from other co-authors.

Declaration of competing Interest. One of the (co-)authors is a member of the editorial board of *Atmospheric Chemistry and Physics*. The peer-review process was guided by an independent editor, and the authors have also no other competing interests to declare.

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