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Seasonal and diel patterns of biogenic volatile organic compound fluxes in a subarctic tundra

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HIGHLIGHTS

- Ecosystem- and branch-level BVOC fluxes were measured using PTR-TOF-MS.
- Net emissions dominated subarctic ecosystem BVOC fluxes.
- Net deposition occurred mainly at night for few oxygenated short-chain compounds.
- Large seasonal and species differences occurred in emission rates and composition.
- Temperature responses for many BVOCs were stronger than previously assumed.

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ABSTRACT

In arctic and subarctic regions, rapid climate changes enhance biogenic volatile organic compound (BVOC) emissions from vegetation, with potentially significant influence on atmospheric processes. However, the seasonal and diel patterns of bidirectional exchange (flux) of BVOCs remain poorly studied in these regions. Here, we deployed a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) to investigate ecosystem-level BVOC fluxes over a growing season in a subarctic tundra heath in Abisko, Northern Sweden, and to quantify BVOC emissions from two widespread dwarf shrubs in the high latitudes, Salix myrsinites and Betula nana. As expected, ecosystem fluxes of short-chained oxygenated compounds (e.g., methanol, acetaldehyde and acetone) and terpenoids (e.g., isoprene, monoterpenes and sesquiterpenes) followed different seasonal and diel patterns. For the short-chained oxygenated compounds, net emissions dominated and peaked in the early growing season, while net deposition occurred sporadically, particularly at night. In contrast, terpenoids were almost exclusively emitted from the ecosystem, with maxima occurring in the peak growing season. At the branch level, these compound groups were emitted from both S. myrsinites and B. nana in clear diel patterns with high emissions during the day. S. myrsinites was dominated by isoprene emissions whilst B. nana was dominated by terpene emissions. Methanol, acetaldehyde and acetone were emitted at comparable levels and similar patterns from both species. Both ecosystem fluxes and branch emissions responded exponentially to enclosure temperature and depended on light levels. Compared to the BVOC emission models, however, the temperature responses were steeper for isoprene, monoterpenes, methanol and acetone, but weaker for sesquiterpenes. Apart from the well-known compounds, many other BVOCs, such as some carbonyls and nitrogen-containing compounds, were emitted from both the ecosystem and plants with significant contributions to the season variation in ecosystem fluxes. Overall, our study highlights the complexity of subarctic ecosystem BVOC fluxes, which vary both seasonally and diurnally. Vegetation composition changes triggered by climate change will shift BVOC composition, with important implications for atmospheric processes and local climate.
1. Introduction

Biogenic volatile organic compounds (BVOCs) emitted from terrestrial vegetation are a major source of reactive organic carbon to the atmosphere (Kramshøj et al., 2016; Peñuelas et al., 2014). BVOCs consist primarily of isoprenoids (e.g., isoprene, monoterpenes, and sesquiterpenes), benzenoids, and some oxygenated compounds (e.g., methanol, acetaldehyde, and acetone) (Peñuelas and Staudt, 2010). These compounds can be highly reactive in the atmosphere (Ortega et al., 2007) and therefore, are of paramount importance to atmospheric chemistry and the climate. Specifically, upon oxidation in the atmosphere, BVOCs can participate in the formation of secondary organic aerosols, which can eventually contribute to cloud formation (Scott et al., 2014). They can also contribute to the production of tropospheric ozone, which is a serious secondary air pollutant harming ecosystem productivity and human health (Demers et al., 1996). In addition, BVOCs can indirectly lengthen the lifetime of methane by reducing concentrations of the hydroxyl radical, which acts as the primary cleansing agent for the atmosphere (Lelieveld et al., 2008; Peñuelas and Staudt, 2010).

Apart from playing important roles in atmospheric processes, BVOCs can mediate multiple ecological interactions in the biosphere. For instance, BVOCs have repeatedly been demonstrated to be involved in multi-trophic interactions among plants, pollinators, herbivorous insects, natural enemies of herbivorous insects (e.g., predators and parasitoids), and both beneficial and antagonistic microbes, as well as between- and within-plant communication (Müller et al., 2022; Taka-bayashi and Shiojiri, 2019). Furthermore, some BVOCs can protect plants from the oxidative stress caused by biotic and abiotic stressors (e.g., herbivore feeding, high temperature), by functioning as antioxidants and maintaining the integrity and fluidity of cell membranes (Peñuelas and Staudt, 2010).

The arctic regions cover approximately 4% of the Earth’s surface and play a key role in the global climate, because of their ability to reflect and absorb solar radiation (Ebert et al., 1995). However, global climate change is causing the Arctic to warm at twice the rate of the rest of the world (IPCC, 2021). As a consequence, increasing temperatures lead to decreasing sea ice and snow cover (IPCC, 2021), which can, in turn, reduce the net reflectance of incoming radiation, and thus amplify the arctic warming. Tundra vegetation composition and productivity are also responding rapidly to climatic warming in the Arctic, with a pervasive trend towards more productive woody vegetation as shrubs expand northward and replace graminoids (Heijmans et al., 2012; Myers-Smith et al., 2020). Furthermore, arctic warming and associated permafrost thaw are altering soil microbial composition and increasing microbial activity, which can, in turn, increase microbial decomposition of soil organic matter and thus augment soil nutrient availability for vegetation growth (Heijmans et al., 2022).

Rapid arctic warming and associated changes in vegetation and soil characteristics have the potential to affect BVOC emissions from arctic ecosystems. Indeed, both the enclosure measurements at the branch and microcosm levels and the eddy covariance measurements at the ecosystem levels have shown that arctic ecosystems are potentially a microcosm levels and the eddy covariance measurements at the branch and microcosm levels and the eddy covariance measurements at the ecosystem levels have shown that arctic ecosystems are potentially a microcosm of the future atmospheric BVOCs emissions. Earlier studies in these regions have predominantly applied snapshot measurements coupled with off-line BVOC analysis techniques, and have thus provided limited information of the BVOC flux dynamics. In addition, most of these studies have solely estimated BVOC emissions, with only a few also considering deposition. Furthermore, measurements of BVOC fluxes in the arctic ecosystems have focused on terpenoid emissions (Faubert et al., 2010; Svendsen et al., 2016; Valolahiti et al., 2015) while the bidirectional exchange and chemical diversity of other BVOCs have largely been ignored. The lack of characterization of flux dynamics of a wider range of BVOCs is likely due to the relatively low sensitivity and mass resolution of gas chromatography-mass spectrometry, which is the current gold standard in BVOC analysis. Nevertheless, recent studies using high resolution and sensitivity proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF-MS) have shown a clear potential for short-chained oxygenated compound fluxes (Baggesen et al., 2021; Seco et al., 2020), implying a need to shift focus away from solely examining terpenoids, to the full spectrum of BVOCs.

Here, we measured diurnal patterns of bidirectional BVOC exchange of a subarctic heath ecosystem over the growing season and characterized the diel emission dynamics of the two predominant deciduous dwarf shrubs in these ecosystems, Salix myrsinites L. and Betula nana L. The deciduous shrubs are large contributors to the arctic greening with ongoing climate change (Elmendorf et al., 2012) and are thus, of our primary interest for projections of future BVOC fluxes. The ecosystem measurements covered a full growing season, from snow melt (late May) until leaf senescence (early August). We deployed a high resolution and sensitivity PTR-TOF-MS and sampled concentrations and BVOC fluxes covering a wide mass range (30–347 a.m.u.), to investigate the temporal dynamics of BVOC fluxes. We hypothesized that: (1) the exchange direction and magnitude of ecosystem BVOCs will vary substantially over the growing season, depending on the identity of individual BVOCs; (2) the composition of ecosystem and branch BVOCs will vary substantially among different plant growth stages and between plant species, respectively; (3) ecosystem BVOC fluxes and branch BVOC emissions will vary seasonally and/or diurnally, tracking the variation in temperature and light intensity.

2. Materials and methods

2.1. Experimental site

The experimental site was located on a wet, subarctic heath in Abisko, northern Sweden (68°210N, 18°490E, 385 m a.s.l.). Mean annual temperature (1986–2015) is 0.2 °C (Abisko Scientific Research Station, 2016), with July and February being the warmest (11.9 °C) and coldest (−10.0 °C) months, respectively. Mean annual precipitation (1986–2015) is 370 mm. Snowmelt occurs from late April to mid-May, and the snow-free period typically lasts from late May until early October. From early June to mid-July, daylight persists for 24 h. Evergreen and deciduous shrubs, graminoids, and herbs dominate the vegetation, while mosses and lichens cover the ground layer. The plant-growing season is from early June to late August.

2.2. Ecosystem BVOC flux measurements

Flux measurements were conducted in the 2017 growing season using a dynamic enclosure technique coupled to a high-resolution proton-transfer-reaction time-of-flight mass-spectrometer (PTR-TOF-MS, PTR-TOF 1000 ultra, Ionicon Analytik). The measurements were carried out in four experimental plots belonging to a long-term climate manipulation experiment. Three plots had been subjected to long-term treatments with warming, litter addition, and their combination, respectively. During the measurement periods, however, there were no
significant temperature differences among plots (daytime/nighttime means ± 1 SD (n = 5 campaigns): control: 16.2 ± 3.6 °C/7.3 ± 3.5 °C, warming: 15.9 ± 4.3 °C/7.8 ± 3.5 °C, litter addition: 16.3 ± 3.5 °C/7.2 ± 3.5 °C, warming and litter addition: 16.3 ± 4.4 °C/7.9 ± 3.7 °C). Therefore, we present all data summarized across the treatments. The reason is that we only have one true replicate per treatment, and the treatment effects have been assessed in a previous study (Baggesen et al., 2021).

Here, we aimed to investigate the seasonal and diel dynamics of the BVOC fluxes in the studied ecosystem with data representing an average response to variable current and future climate conditions. Each plot consisted of a metal frame (22 × 22 cm) installed 10 cm down into the ground in 1999, to allow for ecosystem measurements of gas fluxes. Evergreen and deciduous shrubs dominated the vegetation inside the plots, with litter and mosses covering the ground layer, and B. nana and Salix spp. were only deciduous shrubs present in the plots (Table S1).

For flux measurements, transparent polycarbonate chambers (wall thickness 2 mm, 22 × 22 × 20 cm width × depth × height, volume 9.68 L) were mounted on top of the pre-installed metal frames in the plots. The chambers were continuously flushed with 5.5 L min⁻¹ ambient air taken at a height of 2.3 m (corresponding to 10 times the average canopy height in the area) using oil-free diaphragm pumps. Inside the chamber, a fan circulated the air. The outlets of two chambers and the inlet for ambient air were connected to the PTR-TOF-MS inlet through an automated sampling system. The sampling system consisted of a CR1000 data logger (Campbell Scientific, Logan, Utah) coupled with a digital timer (Wenstronic, Braunschweig, Germany) and a multiple-position PTR-foil solenoid valve (01540-11, Cole-Parmer, Cambridgeshire, UK) that allowed for switching between the two chambers and the ambient air. Each PTR-TOF-MS measurement cycle was completed within 1 h and included three measurements on the ambient (i.e. 00-05, 25–35 and 55–60 min), and on each chamber (chamber 1: 05–10, 20–25 and 40–50 min; chamber 2: 10–20, 35–40 and 50–55 min) (Figure S1). All inlet and outlet lines (1/8 inch I.D., 1/4 inch O.D.) were made of chemically inert perfluoroalkoxy alkanes (PFA) and the outlet lines (14 m long) were continuously heated to prevent water condensation and/or volatile adsorption. To prevent overpressure from accumulating inside the chambers a PFA line (1/8 inch I.D., 1/4 inch O.D.) remained open throughout the measurements.

BVOC mixing ratios from two plots and ambient air were continuously monitored in real-time by PTR-TOF-MS over the course of 24 h and measurements on all four plots were completed within 48 h. Every morning (07:00–09:30, local time) and evening (19:00–21:00, local time), chambers were detached from the plots to remove condensed water on the inside walls of the chambers before placing them on the plots again. Measurements started approximately 1 h after the chambers were attached, to allow for equilibrium to establish. To avoid the direct sunlight causing high water condensation inside the chambers due to enhanced transpiration, and causing high temperature which would in turn stress the plants, we took measurements mainly on cloudy and partially sunny days. We admitted that our measurements may lead to underestimation of ecosystem emissions of those BVOCs that are closely related to vegetation (above vegetation), chamber air temperatures, and relative humidity were recorded every minute during a measurement round. After measurement, the twigs were excised from the plants, the leaves scanned to measure the total leaf area using imageJ, and then oven-dried at 60 °C for three days to determine the dry mass. During measurement, PPFD at the canopy level of each twig was recorded by placing a PAR sensor next to the twig but inside a container to account for the effect of the container on PPFD. Air temperature inside each container, ambient air temperature (1.5 m above vegetation) and relative humidity were recorded every minute using iButtons.

2.3. Branch BVOC emission measurements

Diel patterns of BVOC emissions from two woody shrubs, B. nana and S. myrsinites, present in the experimental plots for ecosystem flux measurements were investigated using PTR-TOF-MS in the period July 21–29. In total, six B. nana and four S. myrsinites plants were measured in five measurement rounds, with each round comprising two plants of the same species and lasting for 24–50 h. In preparation for each measurement round, two plants without visible signs of herbivory and disease were selected. One small twig (~5 cm long) from each plant was enclosed in a transparent polyethylene terephthalate (PET) container (500 mL) placed upside-down over the twig and the opening closed with an aluminum foil lid around the twig. Care was taken to ensure that the plant including the target twig was not wounded during handling. Two PTFE lines for inflow and outflow air, respectively, were inserted to the enclosure from above. A constant stream of zero air (500 ml min⁻¹) (Parker ChromGas Zero Air Generator) was channeled into each container via the inlet line so that a complete exchange of air was achieved within 60 s. Air flow rates were controlled by mass flow controllers (Alicat Scientific). The outlets of both containers were directly connected to the PTR-TOF-MS inlet through an automated three-way valve (01540-11, Cole-Parmer, Cambridgeshire, UK) switching system that alternated between the two containers every 10 min. Each measurement round used new containers and started with background measurements of the empty containers for at least 20 min before the plants were placed in the containers. In addition, blank controls from empty containers supplied with zero air were measured at least once every 12 h during a measurement round. After measurement, the twigs were excised from the plants, the leaves scanned to measure the total leaf area using imageJ, and then oven-dried at 60 °C for three days to determine the dry mass. During measurement, PPFD at the canopy level of each twig was recorded by placing a PAR sensor next to the twig but inside a container to account for the effect of the container on PPFD. Air temperature inside each container, ambient air temperature (1.5 m above vegetation) and relative humidity were recorded every minute using iButtons.

2.4. PTR-TOF-MS analysis

The PTR-TOF-MS measured the mixing ratios of BVOCs at 5-sec intervals across a mass range of m/z 18–347. The drift tube settings were 2.30 mbar and 60 °C (E/N ratio of 120 Td). An internal standard, 1,3-diodobenzene, was continuously added to the instrument drift tube for accurate mass-scale calibration. The PTR-TOF-MS was calibrated once a month with a gas standard (Ionicon, Innsbruck, Austria) diluted in nitrogen using a liquid calibration unit (LCU-a; Ionicon, Innsbruck, Austria). The standard contained a mixture of several volatiles, i.e., acetaldehyde, acetone, acetonitrile, acrolein, benzene, butane, chlorobenzene, crotonaldehyde, dichlorobenzene, ethanol, isoprene, methanol, α-pinene, and toluene, and the final calibration gas concentrations after dilution ranged from 1 to 40 × 10⁻¹⁴ mol mol⁻¹. Due to technical issues, only the calibrations performed on July 4 and August 7 were available (Table S2). Raw PTR-TOF-MS data were processed using the PTRwid software (Holzinger, 2015). PTRwid corrects the mass scale drift, detects and fits ion peaks present in the measured mass spectra, and calculates the mixing ratios of those ion peaks. The mass resolution of the TOF-MS was 1400 m/Δm and the mean mass accuracy of the whole mass spectrum was typically better than 60 ppm, the latter determined by PTRwid comparing all the detected peaks to a library of predefined known ion peaks (Holzinger, 2015). The measured masses were then tentatively assigned in comparison to reference standards and the literature (Vázquez-Serrano et al., 2021). Ions associated with the PTR-TOF-MS ion source or exhibiting poor baselines were excluded from further analysis. For available standard compounds, we obtained the calibration factor for each compound by performing a linear regression between the mixing ratios calculated by PTRwid and the known mixing
ratios generated by the dilution system (Table S2). Then we used the calibration factor to correct the uncalibrated PTR-TOF mixing ratio by multiplying it by the corresponding calibration factor. For other compounds whose standards were not available, the mixing ratios derived from PTR-TOF were used.

In the present study, we reported mainly the compounds [e.g., methanol (m/z 33.03), acetaldehyde (m/z 45.03), acetone (m/z 59.05), isoprene (m/z 69.07), and monoterpenes (m/z 137.127)] we can confidently identify and quantify as these compounds were in our calibration standard mixture and are also the most studied and commonly reported protonated ions detected with the PTR-TOF-MS in the literature (Yáñez-Serrano et al., 2021). Besides these masses, we reported a few other masses that were most influential in determining the differences in BVOC profiles either across the growing season or between the two plant species, to emphasize the importance of other less-reported masses in affecting the BVOC fluxes. Reporting these compounds is relevant to expand the knowledge in the field to novel compounds that might be otherwise ignored.

In order to preclude the carry-over effects of the sampling lines and avoid including peaks due to valve switching, the first and the last 1 min of each measurement period was excluded. For ecosystem flux measurements, the mixing ratios in the ambient air measured directly before and after each chamber measurement were averaged and subtracted from those measured from the chambers in between to obtain a net change in mixing ratios. The ecosystem net flux was then calculated relative to ground surface area (nmol m$^{-2}$ ground area s$^{-1}$) following Ortega and Helmig (2008). Positive values indicate net emissions from the ecosystem to the atmosphere, whereas negative net emissions represent uptake by the ecosystem. It must be noted that for water-soluble, oxygenated volatile compounds, such as methanol and acetone, condensation and deposition on wet chamber surfaces may lead to overestimation of the ecosystem uptake and underestimation of the ecosystem BVOC emissions. For branch emission measurements, the mixing ratios in the blank controls were subtracted from those in branch samples. Emission rates were then calculated relative to the one-sided leaf area (nmol m$^{-2}$ leaf area s$^{-1}$). In order to compare the data obtained in this study with the literature, emission rates of terpenoids normalized to 30 °C and 1000 μmol m$^{-2}$ s$^{-1}$ were calculated according to the algorithms employed in MEGAN2.1 (Guenther et al., 2012).

2.5. Statistical analysis

To characterize differences in ecosystem BVOC fluxes across the season and branch BVOC emissions between plant species, we conducted a Random Forest (RF) between-group classification analysis, as described previously (Ranganathan and Borges, 2010), using the mixing ratios of all reported mass peaks. RF analysis is similar to a principal component analysis but more suitable for nonparametric datasets that comprise many more variables than samples (Ranganathan and Borges, 2010). Differences across the season and between plant species were then visualized using multidimensional scaling (MDS) plots. The importance of each mass peak for the distinction is expressed as the mean decrease in accuracy (MDA) and the odds of the compound being improperly classified is expressed as the out-of-bag (OOB) error rate. Basically, the idea is to measure the decrease in accuracy on OOB data when the values of a given feature are randomly permuted. If the decrease is low, then the feature is not important, and vice-versa. We conducted the RF analysis using the package randomForest in R software (R Core Team, 2020).

3. Results

3.1. Seasonal variation in meteorological conditions and vegetation greenness

During the whole BVOC sampling period, the daytime PPFD (average for 08:00–20:00 period) ranged between 104 and 838 μmol m$^{-2}$ s$^{-1}$ (Fig. 1a) and the daytime average air temperatures ranged between 2 and 20 °C (Fig. 1b). Ecosystem BVOC measurements were mainly conducted on cloudy or partially sunny days, with a daytime mean PPFD and air temperature of 437 μmol m$^{-2}$ s$^{-1}$ and 9 °C, respectively, whilst the branch measurements were conducted on partially sunny or sunny days, with a mean daytime PPFD and air temperature of 754 μmol m$^{-2}$ s$^{-1}$ and 18 °C, respectively. The soil moisture in the experimental plots fluctuated throughout the growing season from 23 to 44 vol % (Fig. 1c). NDVI increased gradually from May and levelled off in July (Fig. 1d), with the lowest and highest NDVI observed around the first and last BVOC sampling campaign, respectively.

3.2. Seasonal and diel changes in ecosystem bidirectional BVOC fluxes

During ecosystem BVOC flux measurements, 218 mass peaks were detected (Table S3). The bidirectional fluxes of these masses varied substantially between sampling campaigns across the growing season, as revealed by the Random Forest classification analysis (Fig. 2a). The first dimension clearly separated BVOC profiles measured on May 28–30 from those measured on Jul 17–18, while the second dimension described the division of these two campaigns from the rest of measurement campaigns. The thirty protonated masses that contributed most to the differences between campaigns included a short-chain oxygenated compound C$_9$H$_{12}$O$_2$ (m/z 75.05), two nitrogen-containing compounds C$_5$H$_4$N$_2$O$_2$ (m/z 76.047) and C$_{10}$H$_{16}$N$_2$ (m/z 84.079), methanol (m/z 33.031), acetone (m/z 59.051), isoprene (m/z 69.07 and 41.034), monoterpenes (m/z 137.127 and 81.069), and sesquiterpenes (m/z 205.187), among others (Fig. 2b).

Most of the fluxes showed net emissions in mid-June and early July when the vegetation was greening up and PPFD and air temperatures were relatively high (Fig. 3 and S2-3). Moreover, the bidirectional fluxes of most of the measured masses exhibited clear diurnal dynamics, the magnitude of which varied across the growing season (Fig. 3 and S2-3; Table S4). Emissions were close to zero during nights, increasing gradually from ca. 05:00 (local time) in the early morning to reach a maximum around 11:00 or 14:00, depending on the compound, and decreasing thereafter. Both seasonal and diurnal variations in mass fluxes followed the variations in enclosure temperatures and PPFD (Figs. 3 and 4).

Methanol (m/z 33.031) fluxes were mainly net emissions, except at nights in early July and early August, during which deposition of up to ~0.05 nmol m$^{-2}$ ground area s$^{-1}$ was observed (Fig. 3c). Net emissions peaked during the day in mid-June (1.4 nmol m$^{-2}$ ground area s$^{-1}$), and remained relatively high at nights (0.3 nmol m$^{-2}$ ground area s$^{-1}$). Then, daytime emissions declined rapidly in early July (0.4 nmol m$^{-2}$ ground area s$^{-1}$), when leaves had fully expanded, although PPFD and enclosure temperatures were both comparable to those in mid-June. Methanol emissions increased exponentially with enclosure temperature in mid-June (Fig. 4a).

Acetaldehyde (m/z 45.028) had a flux pattern similar to methanol (Figs. 3d and 4b). Daytime emissions increased from 0.17 nmol m$^{-2}$ ground area s$^{-1}$ at the end of May to 0.24 nmol m$^{-2}$ ground area s$^{-1}$ in mid-June, then declined rapidly to 0.07 nmol m$^{-2}$ ground area s$^{-1}$ in early July. Unlike methanol, acetaldehyde deposition was only observed during night at the end of May, with the strongest deposition (~0.023 nmol m$^{-2}$ ground area s$^{-1}$) occurring between 02:00–05:00.

Acetone (m/z 59.051) fluxes fluctuated over the growing season between net emissions of up to 0.07 nmol m$^{-2}$ ground area s$^{-1}$, during the day and net deposition of up to ~0.04 nmol m$^{-2}$ ground area s$^{-1}$ at night (Fig. 4e). Emissions were only observed during the day from the end of May to early July, with emissions increasing exponentially with enclosure temperature (Fig. 4e). Deposition occurred in mid-July and early August, concurrently with relatively low PPFD and enclosure temperatures. The highest acetone deposition occurred in early August and was relatively stable through the whole day, although both the
PPFD and enclosure temperatures were not at their lowest.

Another short-chain oxygenated compound $\text{C}_3\text{H}_6\text{O}_2$ (m/z 75.05), which was tentatively identified as acetol, propanoic acid, formic acid ethyl ester, or acetic acid methyl ester, showed net emissions during both daytime and nighttime in all measurement campaigns (Fig. 3i). Emissions peaked in early July, rather than in mid-June, as was observed for methanol, acetaldehyde, and acetone.

The nitrogen-containing compound $\text{C}_5\text{H}_9\text{N}$ (m/z 84.079) showed net emissions but no clear diurnal cycle. Its peak emissions occurred in mid-June and early July (Fig. 3j).

Terpenoid fluxes showed net emissions across the growing season. The ecosystem emission rates of isoprene (m/z 69.07 and 41.034), monoterpenes (m/z 137.12 and 81.069), and sesquiterpenes (m/z 205.187) were low at the onset of plant growth at the end of May (0.03, 0.01, and 0.002 nmol m$^{-2}$ ground area s$^{-1}$, respectively), peaked in early July (0.33, 0.08, and 0.023 nmol m$^{-2}$ ground area s$^{-1}$, respectively), and decreased again in mid-July and early August when PPFD and temperatures decreased (Fig. 3f-h). Terpenoid emissions followed distinct diurnal patterns with maximum emissions around midday and lowest emissions at night. Moreover, terpenoid emissions were strongly dependent on temperatures and PPFD (Fig. 4d-f). When normalized to 30 °C and 1000 μmol m$^{-2}$ s$^{-1}$, the daytime surface emission rates of
isoprene, monoterpenes, and sesquiterpenes averaged 1.33, 0.27, and 0.12 nmol m\(^{-2}\) ground area s\(^{-1}\), respectively, in early July, which corresponds to the peak growing season.

3.3. Diel variation in BVOC emissions from two dominant dwarf shrubs

In total, 347 peaks were detected in branch measurements (Table S5). The Random Forest analysis revealed that volatile profiles of S. myrsinites and B. nana differed markedly from each other, as shown by the two groups separated along the first dimension (Fig. 5a). The continuous variation along the second dimension reflected the diel variation in volatile profiles for each plant species. The between-species difference was most pronounced during the day, while the volatile profiles were relatively similar during night, as revealed by the overlapping emission profiles on the multidimensional scaling plot. The protonated masses that were most influential in distinguishing S. myrsinites from B. nana included isoprene (m/z 69.07 and 41.034), monoterpenes (m/z 137.127 and 81.069), homoterpenes (m/z 151.139 and 219.164), sesquiterpenes (m/z 205.187, 203.17 and 221.176), and several nitrogen-containing compounds (e.g., m/z 70.074, 70.03, and 68.063) (Fig. 5b). In contrast, the oxygenated short-chained volatiles, such as methanol, acetaldehyde, and acetone, were more similar in the volatile profiles, except that methanol was among the most important compounds discriminating between nighttime emissions of the two species (Fig. 5b).

Emissions of all detected masses exhibited distinct diurnal patterns in both species, with high emissions during the day and low emissions at night (Figs. 6–7 and S4-5; Table S6). Isoprene emissions in both species increased exponentially with enclosure temperatures and strongly depended on light levels. Isoprene emissions were close to zero during the night when the PPFD fell below 40 μmol m\(^{-2}\) s\(^{-1}\), and increased gradually with increasing PPFD, reaching a maximum when PPFD and enclosure temperatures peaked. Isoprene was the dominant volatile emitted from S. myrsinites, but a minor compound emitted from B. nana. The mean daytime (08:00–20:00) emission rate of isoprene was 23 times higher in S. myrsinites (7.4 nmol m\(^{-2}\) leaf area s\(^{-1}\)) than in B. nana (0.3 nmol m\(^{-2}\) leaf area s\(^{-1}\)). Once standardized to 30 °C and 1000 μmol m\(^{-2}\) s\(^{-1}\), the daytime isoprene emission rates of S. myrsinites and B. nana were 27.6 and 0.8 nmol m\(^{-2}\) leaf area s\(^{-1}\), respectively. Furthermore, several nitrogenous compounds were characteristic for S. myrsinites. For example, butanenitrile (m/z 70.074) was emitted during the day from S. myrsinites at more than 100-fold higher rates than B. nana (Fig. 6c).

In contrast, other terpenoids were characteristic of the volatile profiles for B. nana. This was particularly the case for homoterpenes and sesquiterpenes (Fig. 6e and f). The mean daytime emission rates of the two homoterpenes 4,8-dimethyl-1,3,7-nonatriene (DMNT, m/z 151.139) and 4,8,12-trimethyltrideca-1,3,7,11-tetraene (TMTT, m/z 219.164), were 8 and 17 times higher in B. nana than in S. myrsinites, respectively. The daytime emission rates of monoterpenes (m/z 137.127 and 81.069) and sesquiterpenes (m/z 205.187, 203.17 and 221.176) were approximately 4 and 2 times higher in B. nana (0.45 and 0.40 nmol m\(^{-2}\) leaf area s\(^{-1}\)) than in S. myrsinites (0.12 and 0.17 nmol m\(^{-2}\) leaf area s\(^{-1}\)), respectively (Fig. 6e). Emissions of monoterpenes, homoterpenes, and sesquiterpenes followed a strong exponential relationship with enclosure temperature and depended on PPFD, whereby no emissions were detected at night between 22:00 and 05:00 (Fig. 7).

Among the short-chain oxygenated volatiles, B. nana emitted greater amounts of acetaldehyde during the day, but similar amounts of methanol and acetone to S. myrsinites (0.33, 1.8, and 0.38 nmol m\(^{-2}\) leaf area s\(^{-1}\) in B. nana, respectively; 0.22, 1.7, and 0.39 nmol m\(^{-2}\) leaf area s\(^{-1}\) in S. myrsinites, respectively) (Fig. 6h–j). During nighttime, however, S. myrsinites sustained higher emissions of methanol than B. nana (0.54 and 0.35 nmol m\(^{-2}\) leaf area s\(^{-1}\), respectively (Fig. 6h). In both species, acetaldehyde and acetone emissions were not detected at night between 22:00 and 05:00, and showed a clear exponential relationship with enclosure temperature (Fig. 7).
4. Discussion

BVOC fluxes in the subarctic heath tundra ecosystem followed distinct seasonal and diel patterns over the growing season. However, different BVOCs behaved differently, with short-chained oxygenated compounds (methanol, acetaldehyde and acetone) showing both net emission and net deposition while terpenoids (isoprene, monoterpenes and sesquiterpenes) almost exclusively showed net emissions, in agreement with reports from a variety of ecosystems worldwide (Seco et al., 2007, 2015, 2020; Wohlfahrt et al., 2015; Sarkar et al., 2020). Likewise, the two dominant woody dwarf shrubs, _S. myrsinites_ and _B. nana_, which contribute to ongoing arctic greening (Elmendorf et al., 2012; Myers-Smith et al., 2020), exhibited clear diel patterns in BVOC emissions and different BVOC compositions. _S. myrsinites_ was characterized by high emissions of isoprene and some nitrogenous compounds, whilst _B. nana_ was characterized by high emissions of monoterpenes, homoterpenes, and sesquiterpenes.

Overall, net emissions dominated for both branch- and ecosystem-scale measurements, but the magnitude of ecosystem net emissions for several well-known BVOCs differed from that previously reported, including those from other arctic and subarctic studies. For instance, ecosystem isoprene emissions in the peak growing season (i.e. in July) were much lower than previously reported (Kramshøj et al., 2016; Lindwall et al., 2016; Holst et al., 2010; Seco et al., 2020, 2022), whereas methanol emissions were either comparable to or higher than previously reported (Holst et al., 2010; Seco et al., 2020). Such discrepancies may be because measurements in the present study were taken on predominantly cloudy and cold days, and because of the different measurement technique. We did not use zero-air in the ecosystem measurements because zero-air creates an artificial concentration gradient that could exaggerate the emissions, and thus our measurements may be more realistic. Furthermore, summer of 2017 was overall relatively cool compared to the average, except for the days where the branch level measurements were performed. The technique used in this study included both long tubing, where compounds such as sesquiterpenes might be adsorbed before reaching the detector (Duhl...
et al., 2008; Kim et al., 2009), and resulted in notable condensation inside the measurement chambers during the long enclosure periods, which has likely caused dissolution of the water-soluble compounds on water films (Seco et al., 2007). Thus, our measurement technique might lead to underestimation of emission rates. Most BVOC fluxes reported in the present study showed clear exponential relationships with enclosure temperatures, particularly on non-cloudy days, and the magnitude of such responses differed substantially among individual BVOCs and from those typically assumed in BVOC emission models such as MEGAN. Ecosystem isoprene fluxes responded more strongly to temperatures than the model assumption, as revealed by the higher beta coefficients observed (0.18–0.22, Fig. 4) compared to the model default (0.13) (Guenther et al., 2012). This agrees with earlier studies in arctic and subarctic ecosystems (Faubert et al., 2010; Holst et al., 2016; Kramshøj et al., 2016; Lindwall et al., 2016; Seco et al., 2020, 2022), together suggesting that isoprene emissions from arctic and subarctic ecosystems are highly sensitive to and will increase further with rising temperature. Interestingly, isoprene responses to temperature at the branch levels (beta = 0.13 for both S. myrsinites and B. nana, Fig. 7) were almost the same as the model default. Monoterpene emissions showed a steeper response to temperature at both ecosystem and branch levels (beta = 0.16–0.18 and 0.14, respectively) than the MEGAN assumes (beta = 0.1), whilst sesquiterpene emissions showed a much weaker response to temperature, particularly at the ecosystem level (beta = 0.002–0.003, and 0.11 for branch measurements) than the MEGAN assumes (beta = 0.17). Likewise, ecosystem methanol and acetone responses (beta = 0.12 and 0.19–0.22, respectively) were stronger than the MEGAN defaults (beta = 0.08 and 0.1, respectively). At the branch level, S. myrsinites and B. nana displayed similar temperature responses to acetone emissions (beta = 0.12 and 0.1, respectively), as predicted by the MEGAN, but differed considerably in terms of methanol emissions (beta = 0.11 and 0.06, respectively). Overall, these observations indicate that the BVOC emission models will underestimate the arctic ecosystem fluxes of isoprene, monoterpenes, methanol and acetone in response to arctic warming, but will overestimate sesquiterpene fluxes, and highlight that arctic BVOC emission models parameterized by locally collected data are in urgent need to more accurately estimate BVOC emission potential under current and future warming scenarios.

4.1. Fluxes of short-chained oxygenated compounds

Methanol emissions from the tundra ecosystem were highest in mid-June, but then plummeted in early July, even though air temperatures and light levels remained largely unchanged. Methanol is produced in plants by the demethylation of pectin, catalysed by endogenous pectin methyl esterase (Fall and Benson, 1996), and is typically emitted during cell wall growth and expansion, with emission declining afterwards (Aalto et al., 2014). In line with these earlier findings, the highest methanol emissions in our study occurred during the periods of vegetation greening and the rapid decline in methanol emissions occurred after leaves had fully expanded. Methanol emissions from ecosystems are most likely driven by plant emissions, as revealed by our branch-level measurements in late July. However, other ecosystem processes, such as leaf senescence, litter decomposition, and soil microbial activity likely also contribute to the ecosystem methanol emissions, particularly in the late growing season. Indeed, previous studies have shown that both soils and decomposing litter are a source of methanol to the atmosphere (Bachy et al., 2016; Gray et al., 2010; Kramshøj et al., 2019). Besides emissions, some methanol deposition was observed at nights in early July. Earlier ecosystem-level studies, including recent ones in subarctic ecosystems, have also observed methanol deposition, but at different times in the growing season (Baggesen et al., 2021; Gonzaga Gomez et al., 2019, 2020; Holst et al., 2016; Seco et al., 2020). This suggests that ecosystem methanol deposition is highly variable, context/ecosystem-dependent, and less predictable than methanol emissions.

Acetaldehyde fluxes showed a similar pattern to methanol, with daytime and nighttime net emissions, both peaking in mid-June when plants underwent rapid growth. While daytime ecosystem emissions of acetaldehyde likely originate mainly from plants, as suggested by previous studies (Gonzaga Gomez et al., 2019; Seco et al., 2020) and our branch measurements, nighttime emissions may come from other sources, such as soils (Bachy et al., 2016). This is supported, to some extent, by our observation of no acetaldehyde branch emissions from plants at night. Furthermore, ecosystem acetaldehyde fluxes showed a strong deposition at night at the end of May, which coincided with the lowest temperature. This agrees well with recent eddy covariance flux measurements conducted nearby our experimental site, showing the strongest acetaldehyde deposition occurring at air temperatures below 3 °C (Seco et al., 2020).

Acetone fluxes fluctuated substantially across the growing season, with emissions dominating during daytime early in the season and deposition dominating during nighttime across the entire season as well as during the daytime late in the season. Our observations generally agree with a previous study reporting acetone emissions during the day and deposition during the night (Seco et al., 2020), whereas another study reported no clear diel flux patterns (Holst et al., 2010). Acetone deposition has been ascribed to its high water solubility resulting in dissolution in dew or entrapment inside stomata (Seco et al., 2007). The high water solubility of acetone cannot fully explain the consistent acetone deposition we observed during the night across the whole
The terpenoids studied here had the highest emission rates in early July, the opposite of short-chained oxygenated compounds, which peaked three weeks earlier in mid-June (Figs. 3 and 6). Thus, the highest terpenoid emissions were registered once leaves were fully grown and during fruiting according to the plant phenology data in Baggesen et al. (2021).

Salix spp. are known to be strong emitters of isoprene (Loreto et al., 2014; Rinne et al., 2009; Svendsen et al., 2016; Vedel-Petersen et al., 2015), as we also observed here for *S. myrsinites*. However, the emission potential of isoprene seems to differ among species. Here, we found that the mean daytime isoprene emission rate of *S. myrsinites* was 7.4 nmol m\(^{-2}\) leaf area s\(^{-1}\), which is nearly one order of magnitude higher than those previously reported for *S. glauca* in Alaska and Greenland (Angot et al., 2020; Krambaj et al., 2016), but similar to those measured with GC-MS in the same species near the experimental site (Swanson et al., 2021). In contrast to isoprene emissions, monoterpenes, homoterpenes, and sesquiterpenes were emitted in higher quantities from *B. nana* than *S. myrsinites*. Unlike monoterpenes and sesquiterpenes, which are emitted constitutively from plants, homoterpenes are typically emitted upon biotic stress, such as insect herbivory (Richter et al., 2016; Ryde et al., 2021). This suggests that the studied plants may have suffered from herbivory stress during the measurement periods, and that biotic stress may be an important source of new compounds released from vegetation into the atmosphere.

If *B. nana* increases in abundance relative to *S. myrsinites* (the main emitter of isoprene), this would result in a shift towards a higher dominance of monoterpene, homoterpene, and sesquiterpene emissions, which have higher secondary organic aerosol (SOA) production potentials than isoprene (Kiendler-Scharr et al., 2009). However, more detailed speciation within these BVOC groups is also important, because structurally similar compounds may have different SOA production potentials (Thomsen et al., 2021). For instance, Thomsen et al. (2021) showed that α-pinene oxidation products contribute to new particle formation to a greater extent than the oxidation products of 3-carene, even though they are both monoterpenes. In this study, we did not measure individual compounds, but another study performed during the same period and at the same site did. Nevertheless, they did not detect 3-carene and only minimal amounts of α-pinene, but various other monoterpenes were identified with different compound compositions across the growing season (Baggesen et al., 2021). Our observations point out that plant species composition and seasonal change/s/phenology are important for the variability in terpenoid speciation.

### 4.3. Fluxes of other compounds

Apart from short-chained oxygenated compounds and terpenoids, many other, less-studied, compounds were also detected in our ecosystem flux measurements (Fig. 3). Some of them showed distinct seasonal and/or diel patterns. For instance, the protonated ion m/z 75.05 ([C\(_2\)H\(_3\)O])\(^+\), which most likely corresponds to acetal, propanoic acid, formic acid ethyl ester, or acetic acid methyl ester (Yáñez-Serrano et al., 2021), showed net emissions from the ecosystem over the season, with maximum emissions occurring in early July. The peak daytime emission rate based on mixing ratios was 1.67 nmol m\(^{-2}\) ground area...
s\(^{-1}\)), which is five times higher than isoprene (0.33 nmol m\(^{-2}\) ground area s\(^{-1}\)). At the branch level, *S. myrsinites* and *B. nana* both emitted m/z 75.05 at rates comparable to monoterpenes (Fig. 6). Both ecosystem and branch emissions of m/z 75.05 followed an exponential relationship with enclosure temperature. Earlier studies have detected both acetaldehyde and propanoic acid in the ambient air of boreal forests (Hellen et al., 2017; Zhou et al., 2017). Our study suggests that vegetation could be an important source of these compounds, particularly during the peak growing season.

In addition, several nitrogen-containing compounds [e.g. m/z 70.074 (C\(_5\)H\(_7\)N) and 84.079 (C\(_4\)H\(_9\)N)] contributed significantly to seasonal variation in ecosystem BVOC fluxes. These compounds were mainly emitted from the ecosystem with emission maxima occurring during the peak growing season. Emissions of the ion m/z 70.074, likely butane nitrile, showed a clear diel pattern, whereas emissions of the ion m/z 84.079 remained relatively constant throughout the day. Both *S. myrsinites* and *B. nana* emitted the ions m/z 70.074 and 84.079 following a diurnal rhythm and temperature dependence, although at different magnitudes. *S. myrsinites* emitted higher amounts of m/z 70.074 and lower amounts of m/z 84.079 than *B. nana*. Again, the observations indicate that plants likely contribute most to ecosystem emission of these nitrogen-containing compounds, but other ecosystem processes (e.g., those occurring belowground) may be a considerable source, especially at night.

In conclusion, although recent decades have witnessed an increasing number of BVOC emission studies from subarctic and arctic ecosystems, real-time measurements using analytical methods with high sensitivity and resolution are still rare. Using PTR-TOF-MS, we present seasonal and diel BVOC fluxes at both ecosystem and branch levels in a subarctic heath ecosystem. We show that BVOC composition varies substantially among different stages of vegetation across the growing season and between the two woody shrubs, *S. myrsinites* and *B. nana*, and that BVOC fluxes follow strong seasonal and diurnal variations. Apart from the commonly-reported BVOCs (e.g., isoprene, methanol, and acetone), our study shows that other, yet-unreported, compounds (e.g., C\(_2\)H\(_4\)O\(_2\), C\(_2\)H\(_6\)N, and C\(_2\)H\(_4\)N) can also contribute to BVOC fluxes in arctic ecosystems. Moreover, our study demonstrates that the temperature responses differ considerably among individual BVOCs, with most showing stronger temperature responses than what the BVOC models typically predict. These results support previous findings showing that arctic BVOC emissions will increase faster than previously thought with the ongoing climatic warming.

**CRediT authorship contribution statement**

Tao Li: Conceptualization, Methodology, Investigation, Formal analysis, Supervision, Funding acquisition, Project administration, Writing – original draft, Writing – review & editing. Nanna Baggesen: Investigation, Data curation, Formal analysis, Writing – review & editing. Roger Seco: Data curation, Formal analysis, Writing – review & editing. Riikka Rinnan: Conceptualization, Supervision, Funding acquisition, Project administration, Writing – review & editing.

**Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Data availability**

Data will be made available on request.