Biogenic Volatile Organic Compounds in Arctic Soil
A Field Study of Concentrations and Variability With Vegetation Cover
WesterLarsen, Lærke; Kramshøj, Magnus; Albers, Christian N.; Rinnan, Riikka

Published in:
Journal of Geophysical Research: Biogeosciences

DOI:
10.1029/2019JG005551

Publication date:
2020

Document version
Publisher's PDF, also known as Version of record

Citation for published version (APA):
RESEARCH ARTICLE

10.1029/2019JG005551

Key Points:
- Biogenic volatile organic compound concentrations varied in soil under different vegetation types in an arctic heath ecosystem.
- Soil BVOC concentrations sampled along a transect with mixed vegetation were related to the vegetation composition.
- Within one day after installation of a soil probe, soil BVOC concentrations returned to a non-disturbed state.

Supporting Information:
- Supporting Information S1

Correspondence to:
R. Rinnan, riikkar@bio.ku.dk

Citation:

Received 31 OCT 2019
Accepted 28 MAY 2020
Accepted article online 9 JUN 2020

Author Contributions:
Conceptualization: Magnus Kramshøj, Christian N. Albers, Riikka Rinnan
Formal analysis: Lærke Wester-Larsen
Funding acquisition: Riikka Rinnan
Investigation: Lærke Wester-Larsen, Magnus Kramshøj, Christian N. Albers
Methodology: Magnus Kramshøj, Christian N. Albers
Project administration: Riikka Rinnan
Resources: Christian N. Albers
Supervision: Magnus Kramshøj, Christian N. Albers, Riikka Rinnan
Visualization: Lærke Wester-Larsen
Writing – original draft: Lærke Wester-Larsen
Writing – review & editing: Magnus Kramshøj, Christian N. Albers, Riikka Rinnan

1. Introduction

Studies of biogenic volatile organic compounds (BVOCs) have focused on emissions from aboveground plant parts (Wenke et al., 2010). However, when considering ecosystem BVOC fluxes or BVOC-mediated interactions, aboveground plant parts are not the only contributor. Belowground, BVOC-mediated interactions are as complex as those aboveground and cannot be ignored (Wenke et al., 2010). The soil can function as either a source or a net sink of BVOCs, and the soil BVOC (sBVOC) contribution to the total ecosystem emission to the atmosphere can range from less than 1% to tens of percent (Peñuelas et al., 2014; Tang et al., 2019). In certain conditions and locations, sBVOC emissions can reach the same magnitude as vegetation emissions, as has been shown for Amazonian terra firme soils in the dry season (Bourtsoukidis et al., 2018). Kramshøj et al. (2016) found sBVOC emissions accounted for 20% of the total arctic tundra emissions.

Belowground, sBVOCs have implications for soil nutrient cycling processes (Smolander et al., 2006). Specific BVOCs in the soil air can alter nitrification, nitrogen mineralization, denitrification, and CH4 oxidation by affecting the microbes responsible for these processes (Leff & Fierer, 2008). Furthermore, BVOCs have been found to reduce the activity of enzymes crucial in carbon, nitrogen, phosphorus, and sulfur cycling in the soil (Adamczyk et al., 2015).

The gaseous BVOC pool in the soil is determined by the sum of sinks and sources, which are influenced by a range of biotic and abiotic factors in the soil environment (Peñuelas et al., 2014). The major biotic sources contributing to the sBVOC pool are roots and microorganisms, while abiotic sources include volatilization of BVOCs from plant litter or soil solution (Peñuelas et al., 2014), along with desorption from soil organic matter (SOM) or soil minerals (Breus & Mishchenko, 2006). Biotic sinks of sBVOCs are primarily microbes that use BVOCs as a carbon and energy source (Albers et al., 2018; Kramshøj et al., 2018). Abiotic sinks include sorption to soil minerals or SOM and dissolution in soil water (Breus & Mishchenko, 2006) as well as abiotic degradation processes (Insam & Seewald, 2010).
The relative importance of the different BVOC sources as well as their changes over time is poorly understood (Asensio, Owen, et al., 2008). Most research on sBVOCs has focused on emissions, measured either from excavated soil samples in laboratories (Bourtouskidis et al., 2018; Kramshøj et al., 2018; Leff & Fierer, 2008) or from soil surfaces, with or without a litter layer, in the field (Asensio, Peñuelas, et al., 2008; Kramshøj et al., 2016). Only few studies have examined BVOC concentrations in the soil, and sampling methods are not well established yet (Albers et al., 2011; Mäki, 2019; Smolander et al., 2006). A major concern associated with sampling in the soil environment is that sampling procedures may cause disturbance that affects the measured concentrations (Van der Putten et al., 2001). Thus, biological and environmental functions of sBVOCs, along with their quantity and blends, are not yet well understood (Peñuelas et al., 2014).

One factor influencing sBVOC blends, either directly or indirectly, may be vegetation cover. BVOCs emitted by plants are important for plant physiology and ecology (Peñuelas & Llusia, 2001). Foliar BVOC emissions vary between species in quantity and composition (Karl et al., 2009), and it is likely that such differences also apply to direct plant root or litter emissions. Furthermore, indirect links between the vegetation cover and sBVOC blends may exist, via rhizospheric interactions. Different plant species support different microbial biomass quantities and microbial communities in the soil, even on a very local scale (Wardle, 2002). Thus, plant species composition might also impact the microbial production or uptake of sBVOCs. For example, different mycorrhizal fungi and other root associated microorganisms emit different BVOCs (Bäck et al., 2010).

Our main aim was to assess how different vegetation covers affect sBVOC concentrations and compositions. An arctic heath served as a suitable location for these in situ measurements thanks to its simple ecosystem structure with a single layer of dwarf shrubs and graminoids above mosses and lichens. Thus, we investigated the differences in sBVOC blends in a low Arctic heath ecosystem below different dominant vascular plant species: Betula nana, Cassiope tetragona, Empetrum nigrum, and Salix glauca as well as along a transect with mixed vegetation cover. We also collected data for a range of environmental variables, such as soil temperature, soil moisture, and pH, in order to assess the importance of these variables on the variation in sBVOC concentrations in soil air. During the first sampling year, we discovered that installation of sampling equipment had a considerable effect on the sBVOC profiles. Therefore, we specifically assessed the installation effects in the following year by comparing the sampling right after the installation to the following sampling. Our hypotheses were as follows: (1) sBVOCs differ in quantity and composition in soil under plots dominated by different plant species; (2) regardless of vegetation, sBVOC concentrations covary with environmental variables; and (3) disturbance of the soil environment by installation of sampling equipment temporarily increases concentrations of some sBVOCs, leading to altered sBVOC composition and increased total concentration.

2. Materials and Methods
2.1. Study Site and Overview of Experiments
The study was conducted in Blæsødaleen located on the southern coast of Disko Island in Western Greenland (69°15′54″N, 53°28′00″W) during the summer months of 2015–2017. Mean annual soil temperature at 5 cm depth is 0.9°C (1991–2004) (Hansen et al., 2006; Hollesen et al., 2015). Annual mean air temperature is −3°C, mean air temperature in July is 7.9°C (Hollesen et al., 2015), and yearly precipitation is 417 mm (2011−2017) (Greenland-Ecosystem-Monitoring, 2019).

Measurements were conducted within an area spanning approximately 250 m² on a tundra heath, dominated by deciduous dwarf shrubs Betula nana L. (from hereon: Betula), Salix glauca L. (Salix), and evergreen low shrubs Cassiope tetragona D. Don (Cassiope) and Empetrum nigrum L. (Empetrum). An overview of the established plots and sampling is presented in Table 1.

Installation disturbance effects were assessed in 2015 and 2016. In 2015, we installed soil probes in Betula, Cassiope, Empetrum, and Salix-dominated vegetation, six probes per vegetation type. Immediately after probe installation, soil air was sampled. There were no further measurements in these plots. In 2016, we established five new plots in each vegetation type. These plots were first used to assess the effects of installation by sampling on the installation date and 1- to 3-day postinstallation. Then we used the plots to study
differences in soil air BVOC concentrations under different dominant plant species by sampling three to four additional times (see Table 1 for specific dates). In 2017, we continued the assessment of plant species effects in the Betula plots from previous year and 10 newly established plots and in a new site with 15 newly established Salix plots with five measurements during July (Table 1). These plots were not sampled for installation effects.

In 2015, a transect was set up in an area with variations in vegetation cover but equal elevation (Figure S1 in the supporting information). Soil probes were systematically installed at 4-m intervals, with 10 probes forming a 36-m-long transect. Soil air was sampled along the transect seven times in the growing season 2016 (Table 1).

### 2.2. BVOC Sampling

Custom-made probes consisting of 25-cm-long pieces of Teflon tubing (6-mm outer diameter, 4-mm inner diameter), fitted with 17-mm brass filters (Propartner, Denmark) in one end were installed in 15-cm depth in the soil. During sampling, adsorbent cartridges containing 150 mg Tenax TA and 200 mg Carbograph ITD (Markes International Limited, Llantrisant, UK) were attached to the probes with a small piece of Viton tubing. A membrane pump (210-1003MTX Twin Port Pocket Pump, SKC) was used to sample soil air at a flow rate of 200 ml min⁻¹ for a total volume of 1.5 L of soil air. Prior to sampling, the air volume in the sampling probe (4 ml) was flushed with 200-ml soil air. PTFE filters with a 0.45-μm pore size (Midisart 2000, Sartorius, Germany) were placed between the probe and adsorbent cartridge to avoid dust particles from entering the cartridge. To ensure that the sampled BVOCs originated from the soil air, and not atmospheric air, the CO₂ concentration in the sampled gas was monitored continuously using a CO₂-gas analyzer (IAQ-Calc, TSI, Minneapolis, MN). As the monitored soil CO₂ concentrations were several times higher than atmospheric air concentrations and remained stable during sampling, we conclude that atmospheric air did not enter the sampled soil air to any significant extent (see also Table S1 for sampled soil air volumes calculated based on soil porosity and water content). In addition to soil CO₂ concentrations, soil temperature at 7-cm depth and soil moisture at 0- to 6-cm depth were manually measured simultaneously with each sBVOC sampling.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Overview of the Established Plots and Sampling Dates in 2015, 2016, and 2017 for the Transect, Betula, Salix, Cassiope, and Empetrum Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site</td>
<td>No. of plots</td>
</tr>
<tr>
<td>Transect Betula</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>Established and sampled 28 August</td>
</tr>
<tr>
<td>5</td>
<td>Established and sampled 21 July, sampled also 22, 25, 26, and 30 July and 2 August</td>
</tr>
<tr>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Salix</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Established and sampled 23 July, sampled also 25, 26, and 30 July and 2 August</td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Cassiope</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Established and sampled 21 July, sampled also 22, 25, 26, and 30 July and 2 August</td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Empetrum</td>
<td>6</td>
</tr>
<tr>
<td>5</td>
<td>Established and sampled 22 July, sampled also 26 and 29 July and 1 August</td>
</tr>
</tbody>
</table>
| *Assessment of installation disturbance effects.*
sampling 25 cm from the soil air sampling probe (ML3 Theta Probe Soil Moisture Sensor, Delta-T Devices, Cambridge, UK). Sampling always took place in the time period 09:00–17:00. Following sampling, the adsorbent cartridges were stored at 5°C for 1–2 months, before being transported to Copenhagen for analysis.

In addition to the soil air measurements, we also sampled atmospheric air on a few occasions. The sampling was done similarly to the soil BVOC sampling, with the same sampling probe, flow rate, and duration; only here the sampling probe was placed 10–15 cm above the vegetation. None of the major soil air compounds were consistently found among the atmospheric air samples. This demonstrates that the sampling probe itself was not polluting the soil air samples to any significant extent, which is important from a methodological point of view.

2.3. BVOC Analysis
sBVOCs were analyzed by gas chromatography-mass spectrometry (GC-MS; 7890A Series GC coupled with a 5975C inert MSD/DS Performance Turbo El System, Agilent). Compounds collected in the adsorbent cartridges were thermally desorbed (UNITY2, Markes International) at 250°C for 10 min, cryofocused at −10°C, and injected onto an HP-5 capillary column (50 m × 0.2 mm; film thickness, 0.5 μm) with helium as carrier gas. The column temperature was held at 40°C for 1 min and then increased by 5°C min⁻¹ to 210°C, and again by 20°C min⁻¹ to 250°C.

Chromatograms were modeled using PARADISe software (Johnsen et al., 2017). Compounds were identified using pure standards (Table S2) or tentatively identified based on mass spectra similarity in the NIST 2014 mass spectral data library, while quantification was performed using pure standards. When a pure standard was not available, α-pinene was used for monoterpenes, α-humulene was used for sesquiterpenes, and toluene was used to quantify other compounds. Compounds were assigned to one of the following 12 chemical groups: aldehydes, alcohols, alkanes, alkenes, benzenoids, esters/acids, ethers, isoprene, ketones, monoterpenoids, nitrogen-/sulfur-/halogenated compounds, and sesquiterpenoids. Tentatively identified compounds with a Match Factor in NIST below 800 (according to the NIST Mass Spectrometry Data Center, Match Factors >800 are referred to as a good match) were denoted unknown but still assigned to a chemical group based on the suggested compound name, for example, unknown alcohol. Therefore, the chemical groups are tentative as the groups contain compounds identified tentatively. Furthermore, if more than one compound was identified with the same name, the compound with the highest match factor was assigned the compound name, and the other listed as unknown.

2.4. Vegetation Analysis
The point intercept method (Jonasson, 1988), where plant species abundance is registered in a defined grid, was used to estimate the percentage cover of plant species present in a 70 × 70 cm area above the gas sampling probe along the transect. The distribution of plant species in each plot can be found in Supplementary Table S3.

2.5. Environmental Properties
Soil core samples were taken from the top 10 cm of the soil, excluding the litter layer, after the last sBVOC sampling. pH was determined using a pH-meter from fresh soil mixed with demineralised water (1:5). SOM was gravimetrically determined from oven-dried soil by loss on ignition at 550°C for 6 hr.

Data on photosynthetically active radiation (PAR), air temperature (2 m above terrain), and liquid precipitation were retrieved from a weather station run by Greenland-Ecosystem-Monitoring (2019; AWS3) situated approximately 150 m from the study area. Data were used to compare the summer seasons among the 3 years in order to assess the possible impact of weather on the sBVOC concentrations (Figure 1).

2.6. Statistics
Paired samples t tests were used to compare sBVOC concentrations on the day of soil probe installation to the first following sampling day in 2016 in order to assess possible effects of disturbance in connection with the installation of the soil probe. For all other analyses, we used nonparametric statistical tests because the sBVOC concentration data did not conform to the requirements of parametric tests. Overall differences along the transect or among vegetation types were assessed with Kruskal-Wallis one-way ANOVA tests. An α value of 0.05 was used. However, for the tests that were performed on each of the 12 sBVOC groups, a Bonferroni corrected α value of 0.004 (0.05 × 12) was used to protect from type I errors. Nonparametric
tests and paired sample t tests were performed using IBM SPSS Statistics Version 25 (IBM Corp., Armonk, NY, USA).

Principal component analysis (PCA) performed on unit-variance scaled data was used to assess grouping of the plots based on the sBVOC concentration patterns and the vegetation composition at the transect and to compare sBVOC compositions on the day of the installation of the soil probes and the following day.

Partial least squares (PLS) regression was used to explore relations between each sBVOC chemical group (Y variable) and environmental parameters (X variables; pH, SOM, soil moisture, soil temperature, and soil CO₂ concentration) across all vegetation types. Y variables were log-transformed prior to the analysis. The one-component PLS models were computed using seven-segment cross-validation for plot mean values of data from the transect and vegetation plots in 2016 and 2017. Only data from the installation day were not included in the analysis. Initially, all X variables were included, and then the model was reduced by excluding X variables based on the variable influence on projection (VIP), which is a weighted sum of squares of the PLS weights and accounts for the amount of explained Y variance in each dimension. The X variables with VIP below 0.5 (unimportant in explaining the Y variable) were excluded, a new model was calculated, and then this variable selection process was repeated until only X variables with VIP above 0.5 were included. The PCA and PLS analyses were done as one component models in SIMCA 3.0.3 (Umetrics, Umeå, Sweden).

### 3. Results

#### 3.1. Effects of Installation Disturbance

The sBVOC blends on the day of the sampling probe installation were in general similar in 2015 and 2016. Of the individual compounds, octadiene and 1-octen-3-ol were found in high concentrations on the day of installation in all vegetation types (Table 2).

Figure 1. Photosynthetically active radiation (PAR), air temperature (2 m above terrain), and liquid precipitation during the growing season in 2015 (a), 2016 (b), and 2017 (c). PAR and air temperature were measured at a weather station approximately 200 m from the BVOC sampling location. Liquid precipitation was measured approximately 2 km from the sampling area at similar elevation. Data were provided by Greenland-Ecosystem-Monitoring, 2019.

**Table 2**

<table>
<thead>
<tr>
<th></th>
<th>Betula</th>
<th>Cassiope</th>
<th>Empetrum</th>
<th>Salix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octadiene</td>
<td>184 ± 53</td>
<td>298 ± 63</td>
<td>89 ± 38</td>
<td>456 ± 124</td>
</tr>
<tr>
<td>1-Octen-3-ol²</td>
<td>59 ± 12</td>
<td>102 ± 56</td>
<td>39 ± 9.5</td>
<td>112 ± 59</td>
</tr>
<tr>
<td>1-Octen-3-one</td>
<td>5.7 ± 1.9</td>
<td>9.6 ± 3.5</td>
<td>6.4 ± 1.9</td>
<td>1.1 ± 0.5</td>
</tr>
<tr>
<td>Nonanal³</td>
<td>3.4 ± 1.4</td>
<td>11 ± 5.2</td>
<td>2.1 ± 0.6</td>
<td>4.6 ± 1.2</td>
</tr>
<tr>
<td>1-Octene⁴</td>
<td>6.1 ± 3.0</td>
<td>7.0 ± 3.9</td>
<td>3.8 ± 1.7</td>
<td>2.8 ± 0.5</td>
</tr>
<tr>
<td>3-Octanone</td>
<td>1.8 ± 1.0</td>
<td>5.8 ± 2.4</td>
<td>1.9 ± 0.8</td>
<td>4.4 ± 1.9</td>
</tr>
<tr>
<td>Octanal⁵</td>
<td>2.6 ± 0.5</td>
<td>4.5 ± 1.0</td>
<td>2.4 ± 0.3</td>
<td>2.4 ± 0.1</td>
</tr>
<tr>
<td>Unknown ketone 2</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>9.0 ± 3.8</td>
</tr>
<tr>
<td>Decanal</td>
<td>1.3 ± 0.7</td>
<td>2.7 ± 1.2</td>
<td>0.6 ± 0.2</td>
<td>3.1 ± 1.1</td>
</tr>
<tr>
<td>Hexanal⁶</td>
<td>1.5 ± 0.7</td>
<td>2.4 ± 1.0</td>
<td>1.1 ± 0.3</td>
<td>2.4 ± 0.6</td>
</tr>
</tbody>
</table>

Note. Values are concentrations in ng L⁻¹ (mean ± standard error; n = 11, except for Cassiope with n = 10); 1-octen-3-ol is an alcohol; octadiene and 1-octene are alkenes; octanal, nonanal, decanal, and hexanal are aldehydes; unknown ketone, 1-octen-3-one, and 3-octanone are ketones. ND = under detection limit.

Compounds identified by pure standards. All other compounds are identified by the NIST 14.0 library.

10.1029/2019JG005551
The most abundant compounds were mainly eight-carbon alkenes, ketones, and aldehydes. The differences between the installation day and the following sampling were further assessed with the 2016 data. PCA showed that sBVOC blends differed between the day of the installation of the soil probes and the following day for all vegetation types (Figure 2a). The first principal component (PC), which explained 64% of the variation in data, mainly described differences in sBVOC blends between vegetation covers, while the second PC (20% explained variance) highlighted the effects of installation. The loading plot showed that the sBVOC blends from the installation day were characterized with relatively higher contributions from alkenes, alcohols, sesquiterpenoids, ketones, and aldehydes compared to the subsequent sampling (Figure 2b).

Total sBVOC concentrations were several-fold higher on the day of installation of soil probes than in the following measurement, regardless of the vegetation type. In the *Emetrum* plots, the sBVOC concentrations were 11-fold higher on the day of installation relative to the concentrations in the following measurement 4 days after (Figure 3b, $P = 0.018$, paired samples t test). In the *Salix* plots, the concentration difference was fivefold (Figure 3c, $P = 0.007$). In *Betula* and *Cassiope* plots, the total sBVOC concentrations were four-fold higher on the day of installation than in the following measurement (Figures 3a and 3d), but these differences were not statistically significant.

Different chemical species caused the increased concentrations upon installation. In the *Cassiope* plots, the concentrations of isoprene and alkenes were significantly higher on the day of installation compared to concentrations sampled the following day (Figure 3, $P < 0.05$, paired samples t test). In the *Emetrum* plots, the concentrations of alcohols, aldehydes, ketones, and monoterpenoids were higher ($P < 0.01$), and in the *Salix* plots, the concentrations of alcohols, aldehydes, alkenes, ketones, and sesquiterpenoids were higher on the day of installation relative to concentrations in the following sampling ($P < 0.05$).

**3.2. Soil BVOC Concentrations Under Different Vegetation Covers**

After the effects of the installation disturbance had abated, the BVOC profiles in the studied soils were overall mainly composed of alkanes, benzenoids, ketones, and aldehydes. In the *Betula, Cassiope*, and *Salix* plots, the sBVOC blend was dominated by alkanes with 28%, 36%, and 48% contribution to the total concentration, respectively. In the *Emetrum* plots, sBVOC concentrations were dominated by aldehydes that comprised 30% of the total.

Cyclopentane, cyclohexane, toluene, and nonanal (the first two identified tentatively and the last two identified by pure standards) were found in high concentrations below all vegetation types in 2016 and 2017. However, we also observed differences between vegetation covers and years. For instance, in both 2016 and 2017, isohexane, heptane, methycyclopentane, and 3-methylhexane (all tentatively identified) were dominant in the *Salix* plots, and either not present or minor components under the other vegetation covers. Concentrations of all compounds can be found in Table S4.
Total concentrations of sBVOCs were significantly higher in the Cassiope and Betula plots than in the Empetrum plots (Figure 4; \( P < 0.05 \), Kruskal-Wallis one-way ANOVA test). Concentrations in the Salix plots were not significantly different from the other vegetation types. Similarly, in 2017 where only Betula and Salix plots were sampled, there were no statistically significant differences in sBVOC concentrations between plots dominated by these two species (Figure S2).

Figure 3. Concentrations of BVOCs in soil below vegetation dominated by (a) Betula, (b) Empetrum, (c) Salix, and (d) Cassiope sampled in 2016. Data are shown for the day of soil probe installation and the first following sampling (1–4 days after). Values are means of all samples (\( n = 5 \)). Error bars show the standard error of mean for the total sBVOC concentrations. Asterisks above bars indicate a statistically significant difference between the total sBVOC concentrations at the two sampling points (\( P < 0.05 \), paired samples \( t \) test).

Figure 4. Concentrations of BVOCs in the soil below vegetation dominated by Betula, Cassiope, Empetrum, and Salix in 2016. The bars represent sBVOC concentrations averaged over the measurement period 22 July to 2 August that excludes the day of installation (\( n = 5 \)). The contributions of each of the BVOC groups is shown, and the error bars represent the standard error of the mean for the total sBVOC concentrations. Different letters above error bars indicate statistically significant differences in total concentration (\( P < 0.05 \), Kruskal-Wallis one-way ANOVA test).
Among the individual BVOC groups, concentrations of aldehydes, alkenes, and ketones were higher in the *Betula* and *Cassiope* plots compared to the *Empetrum* plots ($P < 0.05$, Kruskal-Wallis one-way ANOVA test), while there were no significant differences for other BVOC groups.

In addition to differences in sBVOC concentrations between different vegetation covers, concentrations also varied temporally both regarding the total concentrations and the relative contribution of the different compound groups (Figure 5).

### 3.3. BVOC Concentrations in Soil Air Along the Transect

sBVOC concentrations along the transect were overall dominated by alkanes, aldehydes, benzenoids, and esters/acids (accounting for 24%, 24%, 17%, and 11% of the total BVOCs, respectively). Of the individual compounds, cyclopentane, acetic acid, 2-hexenal, and nonanal (first two tentatively identified and latter two identified by pure standards) were found in high concentrations. Concentrations of all compounds can be found in Table S5. Total sBVOC concentrations were highest at Transect Points 1, 2 and 7, with only minor (statistically insignificant) differences between the other points (Figure 6).

The sBVOC concentrations, as well as their compositions, were partly related to the environmental parameters and the vegetation cover. Transect Points 1 and 2, which had higher sBVOC concentrations (Figure 6) and different compositions from the other transect points (analyzed by PCA, Figure 7), were also characterized as having the lowest SOM content, soil moisture, plant cover, especially that of deciduous plants (Table 3), and the highest soil temperatures during measurements. Transect Point 7 had the second highest concentrations and the most similar sBVOC composition to Points 1 and 2. This point had the highest SOM content of the transect points. Transect Points 3–6 clustered close to each other and were only partly separated from Points 8–10 (Figure 7).
3.4. Environmental Properties and Vegetation Cover

Soil pH differed between vegetation types but stayed similar across years (Table 4). The pH was around 6 in the *Salix* plots and close to 5 in the *Betula*, *Cassiope*, and *Emetrum* plots. SOM content also differed between vegetation types but not between years. SOM content was around 70% in the *Salix* plots, 55% in the *Empetrum* plots, 40% in the *Cassiope* plots, and 20% in the *Betula* plots. Soil CO₂ concentration and soil moisture, measured in connection with the soil air sampling, did not differ consistently between vegetation types. In the transect, soil CO₂ concentration and SOM increased along the transect, peaking at Transect Points 7–8 and then decreasing again at Points 9 and 10. pH decreased along the transect with lowest values at Transect Points 6–8, whereas soil moisture was lowest in Transect Points 1–2 and 7–8.

Concentrations of sBVOCs across the measurements were positively correlated with soil temperature, which was clearly the most important environmental variable explaining the concentrations according to the PLS models (Table 5). Soil moisture positively correlated with the concentrations of isoprene, alcohols, aldehydes, alkenes, ethers, and ketones. SOM content showed negative correlation with the concentrations of alcohols, aldehydes, alkenes, esters and acids, and ketones as well as the N, S, and halogenated compounds (Table 5).

4. Discussion

4.1. Vegetation Cover and sBVOC Concentrations

BVOC concentrations and compositions differed below the different dominant plant species in the low Arctic heath soil. Moreover, differences in the vegetation cover could also, to some extent, explain the concentrations and compositions of BVOCs in the soil along the studied transect. However, the underlying mechanisms are numerous and interlinked.

Our main objective was to assess how sBVOC concentrations differed with different vegetation covers. We found that the total concentration was lower in soil under *Empetrum* than under *Betula* or *Cassiope*. We have not assessed leaf emissions in the present study, but aboveground vegetation BVOC emissions could be hypothesized to be mirrored in root and litter BVOC emissions (Lin et al., 2007). However, previous findings on foliar BVOC emissions from the studied species, *B. nana*, *C. tetractina*, *E. hermaphroditum*, and *S. glauca* (Schollert et al., 2014, 2015, 2017; Vedel-Petersen et al., 2015), do not match the BVOC blends we observed in the soil below plots dominated by these species. In general, the proportion of terpenoids is
much greater in the aboveground BVOC emissions compared to soil BVOC concentrations, which are primarily composed of nonterpenoid compounds. For instance, isoprene, which is the BVOC emitted in highest quantities by the aboveground plant tissue of *S. glauca* (Vedel-Petersen et al., 2015), was only found in minor concentrations in the soil air below the *S. glauca* in our study.

BVOC concentrations sampled in soil air are the sum of all biotic and abiotic processes adding and removing BVOCs to/from the gaseous sBVOC pool (Tang et al., 2019). A high concentration is not necessarily caused by a high production rate but might indicate low breakdown, sorption, or dissolution. In the following discussion, we assess the different sources and sinks that could contribute to the sBVOCs in relation to the vegetation cover.

Leaf and needle litter from different plant species differ in BVOC emissions (Gray & Fierer, 2012; Ramirez et al., 2010; Svendsen et al., 2018). Furthermore, litter emissions are also affected by the microbial community associated with the litter (Gray et al., 2010; Svendsen et al., 2018). Svendsen et al. (2018) found higher BVOC emissions of mainly terpenoids, from *C. tetragona* litter compared to *Salix* spp. litter, but we did not observe similar trends for the sBVOC concentrations below these species.

Similar to the emissions from litter, emissions from plant roots and root associates are species specific, and this could also contribute to differences in sBVOC concentrations below different plant species (Dicke et al., 2003; Peñuelas & Llusia, 2001). The belowground biomass of arctic tundra shrubs exceeds their aboveground biomass (Iversen et al., 2015), and thus, roots play a substantial role here. However, to our knowledge, no available data on root BVOC emissions exist for our studied species.

### Table 3

<table>
<thead>
<tr>
<th>Transect point</th>
<th>pH</th>
<th>SOM (%)</th>
<th>Soil CO₂ (ppm)</th>
<th>Soil M (%)</th>
<th>Soil T (°C)</th>
<th>Deciduous (%)</th>
<th>Evergreen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (0 m)</td>
<td>6.7</td>
<td>4.5</td>
<td>769 ± 16</td>
<td>11 ± 1.5</td>
<td>16 ± 1.0</td>
<td>0.0</td>
<td>64</td>
</tr>
<tr>
<td>2 (4 m)</td>
<td>6.4</td>
<td>5.5</td>
<td>824 ± 42</td>
<td>11 ± 1.8</td>
<td>16 ± 0.9</td>
<td>18</td>
<td>2.0</td>
</tr>
<tr>
<td>3 (8 m)</td>
<td>6.0</td>
<td>7.0</td>
<td>992 ± 51</td>
<td>18 ± 2.7</td>
<td>12 ± 0.5</td>
<td>123</td>
<td>21</td>
</tr>
<tr>
<td>4 (12 m)</td>
<td>6.1</td>
<td>9.0</td>
<td>1,668 ± 47</td>
<td>16 ± 2.5</td>
<td>13 ± 0.5</td>
<td>123</td>
<td>6.0</td>
</tr>
<tr>
<td>5 (16 m)</td>
<td>6.1</td>
<td>10</td>
<td>1,096 ± 125</td>
<td>16 ± 3.3</td>
<td>11 ± 0.5</td>
<td>141</td>
<td>10</td>
</tr>
<tr>
<td>6 (20 m)</td>
<td>5.1</td>
<td>25</td>
<td>1,705 ± 106</td>
<td>15 ± 2.9</td>
<td>12 ± 0.4</td>
<td>27</td>
<td>99</td>
</tr>
<tr>
<td>7 (24 m)</td>
<td>5.4</td>
<td>41</td>
<td>1,829 ± 70</td>
<td>13 ± 2.7</td>
<td>12 ± 0.5</td>
<td>110</td>
<td>3.0</td>
</tr>
<tr>
<td>8 (28 m)</td>
<td>5.0</td>
<td>26</td>
<td>2,169 ± 128</td>
<td>12 ± 2.5</td>
<td>12 ± 0.5</td>
<td>148</td>
<td>1.0</td>
</tr>
<tr>
<td>9 (32 m)</td>
<td>5.6</td>
<td>17</td>
<td>1,481 ± 69</td>
<td>15 ± 2.3</td>
<td>12 ± 0.5</td>
<td>123</td>
<td>0.0</td>
</tr>
<tr>
<td>10 (36 m)</td>
<td>5.8</td>
<td>11</td>
<td>832 ± 21</td>
<td>22 ± 3.3</td>
<td>14 ± 0.5</td>
<td>84</td>
<td>0.0</td>
</tr>
</tbody>
</table>

*Note.* Values are mean ± standard error for all samplings. For soil CO₂, soil M and soil T (*n* = 6–8).

### Table 4

<table>
<thead>
<tr>
<th>Year</th>
<th>Vegetation</th>
<th>pH</th>
<th>SOM (%)</th>
<th>Soil CO₂ (ppm)</th>
<th>Soil M (%)</th>
<th>Soil T (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2015</td>
<td>Betula</td>
<td>5.1 ± 0.1</td>
<td>19 ± 4.5</td>
<td>2,091 ± 251</td>
<td>19 ± 0.7</td>
<td>8.2 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Cassiope</td>
<td>5.4 ± 0.1</td>
<td>40 ± 5.3</td>
<td>1,056 ± 35</td>
<td>35 ± 2.4</td>
<td>5.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Empetrum</td>
<td>4.7 ± 0.1</td>
<td>59 ± 9.9</td>
<td>906 ± 29</td>
<td>29 ± 2.7</td>
<td>5.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Salix</td>
<td>5.9 ± 0.1</td>
<td>73 ± 6.1</td>
<td>1,566 ± 139</td>
<td>20 ± 0.7</td>
<td>7.2 ± 0.1</td>
</tr>
<tr>
<td>2016</td>
<td>Betula</td>
<td>ND</td>
<td>ND</td>
<td>1,562 ± 148</td>
<td>14 ± 0.9</td>
<td>12 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Cassiope</td>
<td>5.4 ± 0.2</td>
<td>40 ± 4.2</td>
<td>1,536 ± 39</td>
<td>21 ± 1.3</td>
<td>13 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Empetrum</td>
<td>4.9 ± 0.2</td>
<td>52 ± 8.8</td>
<td>1,563 ± 115</td>
<td>20 ± 1.7</td>
<td>12 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Salix</td>
<td>6.1 ± 0.1</td>
<td>59 ± 3.5</td>
<td>1,849 ± 60</td>
<td>16 ± 0.9</td>
<td>14 ± 0.3</td>
</tr>
<tr>
<td>2017</td>
<td>Betula</td>
<td>5.4 ± 0.1</td>
<td>20 ± 1.8</td>
<td>1,048 ± 80</td>
<td>17 ± 2.9</td>
<td>8.3 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Salix</td>
<td>6.0 ± &lt;0.1</td>
<td>79 ± 1.9</td>
<td>1,781 ± 258</td>
<td>12 ± 1.3</td>
<td>8.1 ± 0.4</td>
</tr>
</tbody>
</table>

ectomycorrhizal fungal species have been shown to emit different BVOCs (Bäck et al., 2010). Of the species we focused on, B. nana and S. glauca are associated with ectomycorrhizal fungi (Clemmensen et al., 2006), while Cassiope and Empetrum have ericoid mycorrhiza (Iversen et al., 2015). Mycorrhizal differences could affect sBVOCs both directly due to different emissions and indirectly due to effects on soil food web discussed below.

Indirectly, sBVOC concentrations are affected by vegetation cover because the vegetation cover affects the soil food web. Plants release root exudates to the soil, and different plant species exude different quantities and different chemical mixtures of compounds, including secondary metabolites such as phenolics (Jones et al., 2004; Zwetsloot et al., 2018). The root exudates and interactions between organisms in the soil food web affect the composition and biomass of microbial communities (Wardle, 2002). As microbially produced BVOCs are known to differ between species (Effmert et al., 2012; Insam & Seewald, 2010), microbial community differences would thus translate into contrasting microbial BVOC emissions and consumptions below different plant species.

In addition to supporting differences in production and release of BVOCs, the influence of different plant species on soil microbial communities and soil conditions may also affect microbial mineralization of sBVOCs. Arctic soil microbes have been shown to completely mineralize various BVOCs (Albers et al., 2018). This sBVOC uptake process appears to be so efficient that the large release of BVOCs from thawing permafrost was almost completely hindered when the BVOCs needed to pass the active layer soil of arctic tundra before release to the atmosphere (Kramshøj et al., 2018).

In addition to biotic factors, abiotic factors may cause differences between vegetation covers. Differences in the soil physical and chemical environment are known to affect which plant species inhabit the area, for example, pH and soil moisture (Brady & Weil, 2014). In turn, plants may also change the soil environment they inhabit both chemically and physically (Bardgett, 2005). As different soil environments support differences in the microbial community, for example, porosity and soil moisture (Bardgett, 2005), this could contribute to differences in sBVOC concentrations between vegetation types.

Most compounds detected in the soil gas phase were present in low concentrations, but around 25 compounds appeared in concentrations between 2–35 ng L−1. Many of these compounds, such as α-pinene, benzaldehyde, and heptane, are reported to be present in the soil air (Asensio, Owen, et al., 2008), emitted from the soil (Kramshøj et al., 2016, 2019), emitted from vegetation (Faubert et al., 2012), and emitted by microbes (Imperato et al., 2019). The ecological roles of many of these compounds have not yet been established. However, some of the dominant compounds, such as nonanal (Fernando et al., 2006), octanal, and hexanal (Wright et al., 2000), have been shown to have antifungal properties. Butanone may promote plant growth (Jiang et al., 2019), while α-pinene can inhibit it (Singh et al., 2006).

### 4.2. Environmental and Temporal Factors Related to sBVOC Concentrations

Abiotic factors were found to correlate with sBVOC concentrations regardless of plant cover and season. We found a strong positive relationship between soil temperature and sBVOC concentrations, which fits with previous observations of BVOC release from arctic soils (Kramshøj et al., 2019) and from leaf litter (Svendsen et al., 2018). There are two obvious ways, in which an increased temperature could lead to an increased sBVOC concentration: (1) by increased formation of sBVOCs due to increased biological activity
(microbes and roots) and (2) by liberation of adsorbed and dissolved BVOCs due to increased vapor pressure of the BVOCs. Regarding increased biological activity, it is well known that microbial growth and activity are stimulated by warming, which is normally followed by an increase in soil respiration by heterotrophic microorganisms (e.g., Pietikäinen et al., 2005). However, while there was a clear correlation with temperature, there was no correlation between soil CO₂ and sBVOC concentrations, suggesting that the increased temperature was not followed by an increased microbial activity. Increased temperature would also increase BVOC consumption by microbes, but the relative importance of temperature on production versus consumption of sBVOCs is currently unknown. Plant BVOC production increases with temperature (Guenther et al., 1993), but it is not known if BVOC excretion from roots shows a similar increase with temperature. Regarding liberation of bound or dissolved BVOCs, the volatility of all BVOCs increases with temperature (Insam & Seewald, 2010), so if there is a pool of sBVOCs that is not in the gaseous phase, some of this may be released at higher temperature. For hydrophobic sBVOCs like most alkanes and terpenes, especially those with relatively low boiling points, a substantial fraction of the soil pool is probably bound to SOM. For hydrophilic sBVOCs like many alcohols, a substantial fraction is probably dissolved in soil water. In both cases, an increase in temperature would change the partition coefficient between sorbed and/or dissolved BVOCs and gaseous BVOCs and lead to more BVOCs in the soil air (Tang et al., 2019).

We also found positive correlations between soil moisture and concentrations of some sBVOCs. Soil moisture content is one of the most important factors affecting microbial activity (Bardgett, 2005). Faubert et al. (2010) and Faubert et al. (2011) found significant emissions of BVOCs from boreal peatlands with a high water table. Temporal variations in soil moisture have also been found to be related to emissions of sBVOCs to the atmosphere (Bourtsoukidis et al., 2018). The observed negative correlation between SOM and sBVOC concentrations might be linked to higher sorption of sBVOCs in soils with a high SOM content during periods of net BVOC production in the soil (Breus & Mishchenko, 2006). Another possible explanation for this relationship could be higher microbial consumption of sBVOCs in soils with high SOM content (Albers et al., 2018).

Apart from the spatial differences in the sBVOC concentrations, temporal differences were also evident. The sBVOC blends varied both in quantity and quality during each season and between seasons (Figure 5). Due to the relatively short time series and/or factors not accounted for in our study, the cause or causes of these temporal variations in sBVOC concentrations cannot be determined, and future studies could seek to reveal these.

### 4.3. Installation Disturbance

Differences between sBVOC concentrations immediately after installation of the soil probes and the following sampling day were striking. The reasons for the increased concentrations and the differences in the sBVOC blends are likely related to physical disturbance of plant roots, soil structure, and/or microbial communities, for example, fungal hyphae. For example, root cutting may lead to increased root BVOC concentrations, as was found by Hayward et al. (2001) and Ketola et al. (2011). Rinnan et al. (2013) found similar compounds as in our study, for example, 1-octene, to be induced by mechanical disturbance of subarctic heath vegetation. Furthermore, an increase in microbial release of BVOCs caused by an increased input of labile C from damaged roots and microbial communities might also have taken place (Mišik, 2019). Future research is encouraged to take into consideration the disturbance from installation equipment when designing experiments. Based on our results, installation of sampling equipment 1 day prior to sampling seems sufficient to avoid sampling in a disturbed environment.

### 5. Conclusions and Future Directions

We found that sBVOC concentrations varied between plots dominated by different vegetation types in an Arctic heath ecosystem. Total sBVOC concentrations were highest in _Cassiope_ plots (117 ng L⁻¹), followed by _Betula_ (110 ng L⁻¹), _Salix_ (69 ng L⁻¹), and _Empetrum_ (21 ng L⁻¹). Furthermore, sBVOC concentrations sampled along a transect with mixed and varying vegetation cover were also related to the vegetation cover. However, a direct link between the vegetation cover and sBVOC concentrations cannot be assumed, and the underlying mechanisms for these differences need still to be explored by future studies.
Moreover, we stress the importance of avoiding disturbance of the soil environment when sampling sBVOCs. Within 1 day after installation of a soil probe, sBVOC concentrations returned to a nondisturbed state. Thus, sampling of sBVOCs immediately after installation of equipment in the soil should be avoided in future studies.

Our results have shown that sBVOC concentrations vary immensely both on a temporal and a spatial scale. Thus, many replicates on both scales are needed to gain a more accurate representation of sBVOC concentrations.

The individual components of the soil system are difficult to study separately because they are highly interconnected. The distribution of BVOCs in the different compartments of the soil (dissolved, sorbed, and gaseous), and rate of release from these compartments, will differ depending on the compound, due to differences in physicochemical properties. Furthermore, soil environments supporting different plant species may differ in relation to sorption potential and soil moisture. Thus, simultaneous sampling of the different sBVOC compartments would be highly interesting, to get a more detailed overview of the entire sBVOC pool. Moreover, applying a method for separating the pools of sBVOCs regarding their source (microbial, root, etc.) would enable a deeper understanding of the underlying mechanisms. This might be done in future studies, for example, by using stable C isotope signals as has been previously done to separate pools of respiratory CO2 (Formänk & Ambus, 2004) or using inhibitors of specific processes.

Data Availability Statement

The data presented are included in the main text and the supporting information. In addition, we have archived the data in figshare repository (https://doi.org/10.6084/m9.figshare.12085599.v1).

Acknowledgments

The study was financially supported by the Danish Council for Independent Research/Natural Sciences (DFF-4002-00495 and DFF-4181-00141), the Carlsberg Foundation, the European Research Council (ERC) under the European Union’s Horizon 2020 Research and Innovation Programme (Grant Agreement 771012), and the Danish National Research Foundation (CENPERM DNRF100). Data from the Greenland Ecosystem Monitoring Programme were provided by Asiaq—Greenland Survey, Nuuk, Greenland. We thank Arctic Station for the facilities and logistical support in field work, Marie Flyger for assisting field work, and Ida Vedel-Petersen, Goshia Sylvester, and Michelle Schollett for running the GC-MS analyses.

References


Kramshøj, M., Vedel-Petersen, I., Schollett, M., Rinnan, Å., Nymand, J., Ro-Poulsen, H., & Rinnan, R. (2016). Large increases in Arctic biogenic volatile emissions are a direct effect of warming. Nature Genecson, 9, 349, +


