



## **Volatile emissions from thawing permafrost soils are influenced by meltwater drainage conditions**

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1 Volatile emissions from thawing permafrost soils  
2 are influenced by meltwater drainage conditions

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18

## 19 Abstract

20 Vast amounts of carbon are bound in both the active layer and permafrost soils in the Arctic. As a  
21 consequence of climate warming, the depth of the active layer is increasing in size and permafrost  
22 soils are thawing. We hypothesize that pulses of biogenic volatile organic compounds are released  
23 from the near-surface active layer during spring, and during late summer season from thawing  
24 permafrost, while the subsequent biogeochemical processes occurring in thawed soils also lead to  
25 emissions. Biogenic volatile organic compounds are reactive gases that have both negative and  
26 positive climate forcing impacts when introduced to the Arctic atmosphere, and the knowledge of  
27 their emission magnitude and pattern is necessary to construct reliable climate models. However, it  
28 is unclear how different ecosystems and environmental factors such as drainage conditions upon  
29 permafrost thaw affect the emission and compound composition. Here we show that incubations of  
30 frozen B horizon of the active layer and permafrost soils collected from a High Arctic heath and fen  
31 release a range of biogenic volatile organic compounds upon thaw and during subsequent  
32 incubation experiments at temperatures of 10 °C and 20 °C. Meltwater drainage in the fen soils  
33 increased emission rates nine times, while having no effect in the drier heath soils. Emissions  
34 generally increased with temperature, and emission profiles for the fen soils were dominated by  
35 benzenoids and alkanes, while benzenoids, ketones and alcohols dominated in heath soils. Our  
36 results emphasize that future changes affecting the drainage conditions of the Arctic tundra will  
37 have a large influence on volatile emissions from thawing permafrost soils – particularly in  
38 wetland/fen areas.

## 39 Introduction

40 Biogenic volatile organic compounds (BVOCs) released from the Arctic biosphere can  
41 influence chemical and physical properties of the atmosphere having either positive or  
42 negative climate forcing impacts (Arneth et al. 2010). For instance, BVOC emission can  
43 induce the formation of particles in the otherwise unpolluted Arctic air, possibly leading to  
44 increased cloud cover (Paasonen et al. 2013). On the other hand, BVOCs also have the  
45 potential to prolong the lifetime of methane in the atmosphere through the depletion of  
46 hydroxyl radicals via oxidation reactions, thus strengthening the global warming potential of  
47 methane (Peñuelas and Staudt 2010). BVOC emission data from Arctic areas is therefore  
48 essential in order to improve current climate models.

49

50 The Arctic is particularly sensitive to climate changes due to a number of climate change-  
51 related events specific for the Arctic, such as the melting of sea ice that drastically decreases  
52 albedo, and as a consequence, the Arctic is currently experiencing climate warming at twice  
53 the rate compared to the global mean (IPCC, 2013). Over the past three decades, the  
54 temperature in the Arctic has increased by an average of 1 °C per decade, and climate models  
55 predict temperatures in the Arctic to further increase 3–11 °C by 2100 (IPCC, 2013).

56

57 Northern Hemisphere permafrost deposits store more than 1500 Pg of organic carbon  
58 (Tarnocai et al. 2009; Schuur et al. 2015), which is nearly twice the amount of carbon in the  
59 atmosphere and about 50% of the estimated global below-ground organic carbon pool  
60 (Tarnocai et al. 2009). Despite the cold conditions of the Arctic, microorganisms are still  
61 active even at very low temperatures (Panikov et al. 2006; Steven et al. 2008) and slow  
62 decomposition in the permafrost also leads to an accumulation of trace gases trapped in the  
63 soil (Rivkina et al. 2007). With the ongoing warming trend and near-surface permafrost thaw,

64 these compounds can be liberated and released into the atmosphere (Rivkina et al. 2007;  
65 Mackelprang et al. 2011). However, significantly higher trace gas emission occurs when the  
66 microbial activity in the soil increases and previously frozen organic matter, stored for  
67 millennia, becomes accessible for microbial decomposition (Gruber et al. 2004; Osterkamp  
68 2007; Prater et al. 2007; Elberling et al. 2013). During permafrost thaw, greenhouse gases like  
69 carbon dioxide, methane, and nitrous oxide associated with microbial activity and  
70 decomposition processes are released from the permafrost soil (Schuur et al. 2009; Elberling  
71 et al. 2010). However, the emissions of BVOCs from these systems are much less understood.  
72 Recently, it was reported that permafrost may also be an important source of ethanol,  
73 methanol and other compounds (Kramshøj et al. 2018). Kramshøj et al. (2018) showed that  
74 under aerobic conditions BVOCs released from permafrost are almost entirely taken up by the  
75 active layer, suggesting that a climate warming induced BVOC release from thawed  
76 permafrost soils might not be relevant for atmospheric chemistry in the Arctic. However, in  
77 waterlogged conditions, BVOC emission to the atmosphere could be significant as microbial  
78 BVOC consumption is likely to be slowed down due to a low redox potential (Bridgham et al.  
79 1998). Furthermore, permafrost soils are not always covered by an active layer. Along shores  
80 and rivers for example, permafrost soils are exposed and directly in contact with the  
81 atmosphere. Also in thermokarst landscapes and when frost heavings lift up permafrost layers  
82 due to freeze-thaw events, thawing permafrost soils could directly release BVOCs to the  
83 atmosphere.

84

85 BVOCs and their oxidation products can, depending on the chemical environment, facilitate  
86 particle growth in the atmosphere. Due to limited pollution, Arctic air is generally very clean,  
87 and the growth of particles large enough to act as cloud condensation nuclei might therefore  
88 be coupled to BVOC emissions (Paasonen et al. 2013). Increases in BVOC emission from

89 thawing permafrost soils could thus potentially increase particle and cloud formation, which  
90 would increase atmospheric reflectance of sunlight and thus have a cooling impact on the  
91 climate.

92

93 The fate of meltwater, following permafrost thaw, is important because soil moisture is a  
94 main environmental driver of carbon exchange in the tundra (Oechel et al. 1998; Shaver et al.  
95 2006; Oberbauer et al. 2007). Whether a soil ends up being waterlogged or not is of great  
96 importance for the BVOC emissions, as aerobic and anaerobic microbial decomposition  
97 processes lead to the production of different types of compounds (Stotzky et al. 1976). In oxic  
98 soils, the largest source for BVOCs is secondary metabolite production, while BVOC  
99 production under anaerobic conditions is coupled to the energy chain of fermentative  
100 processes. At the same time, soil microorganisms utilize BVOCs as a carbon source (Owen et  
101 al. 2007, Albers et al. 2018); a process likely decelerated in anoxic soils with lower redox  
102 potential (Bridgham et al. 1998). The net emission from soils that become waterlogged will  
103 therefore likely increase in magnitude (Faubert et al. 2010; Faubert et al. 2011). Kramshøj et  
104 al. (2018) studied the release of BVOCs from thawing permafrost soils and found a positive  
105 correlation between soil water content and BVOC release, making the authors suggest that  
106 anoxic waterlogged soils have the highest net production potential.

107

108 Studies from lower latitudes suggest that soil BVOC emissions are usually 1-2 orders of  
109 magnitude lower than emissions from plant canopies (Leff and Fierer 2008; Insam and  
110 Seewald 2010; Gray et al. 2014; Peñuelas et al. 2014), however soil emissions appear more  
111 quantitatively important for Arctic tundra ecosystems (Kramshøj et al. 2016). Kramshøj et al.  
112 (2016) studied BVOC emissions from a Greenlandic tundra heath, and found soil emission  
113 rate to be  $59 \mu\text{g m}^{-2} \text{h}^{-1}$  and account for 20% of the ecosystem emission.

114 In this study, the active layer soil was from the B horizon, that in comparison to the A horizon  
115 contains less organic matter and microbial biomass, which are both important for BVOC  
116 production and consumption processes (Peñuelas 2014). Leff and Fierer (2008) measured the  
117 net emission of BVOCs from 28 soil samples collected in a diverse array of ecosystems and  
118 found a significant positive correlation between BVOC emission and organic carbon content.  
119 Kramshøj et al. (2018) found the organic layer to be a bigger sink for permafrost released  
120 BVOCs than the mineral layer, while the organic and mineral layers had comparable emission  
121 rates but different compound composition.

122 Plant roots and microorganisms are considered the largest BVOC sources in soil (Insam and  
123 Seewald 2010; Peñuelas et al. 2014), while decomposition processes and even abiotic  
124 decomposition can also lead to the release of BVOCs. Similar to the plant canopy, BVOCs in  
125 the soil are produced e.g. as means for intra- and interspecies communication, defense  
126 mechanisms and regulatory effects limiting or stimulating the growth of plants and  
127 microorganisms (Farmer and Ryan 1990; Paré et al. 1996; Farag et al. 2006; Garbeva et al.  
128 2014). In soils without plant roots, the soil microbial community and the biogeochemical  
129 processes therefore determine the type and abundance of BVOCs in the soil (Insam and  
130 Seewald 2010). With temperature being one of the most important factors for the soil  
131 microbial community composition (Deslippe et al. 2012), climate warming will likely affect  
132 the soil BVOC emission profile. In addition, temperature directly affects the vapor pressure of  
133 BVOCs.

134

135 With a focus on Arctic B horizon of the active layer and permafrost soils, the aims of our  
136 work are to assess the quantity and composition of BVOCs released upon thaw, the  
137 temperature dependency of emissions from recently thawed soil, and the importance of  
138 meltwater drainage conditions for emissions upon permafrost thaw. We incubated B horizon

139 and permafrost soils from a wet (fen) and dry (heath) ecosystem in the High Arctic in a  
140 laboratory experiment to test the following hypotheses: 1) Upon thaw, the BVOC release is  
141 larger from permafrost than the B-horizon soils due to a long build-up period and the  
142 compound compositions are different, 2) emission rates increase with increased temperature,  
143 and 3) meltwater drainage impacts the compound composition and decreases the net  
144 emissions from drained permafrost soils compared to waterlogged permafrost soils.



## 145 Materials and methods

### 146 Site description

147 The soils examined in this study were collected at the High Arctic Zackenberg valley, NE  
148 Greenland (74°30' N, 21°00' W), in a wet sedge fen (from here on referred to as fen) and in a  
149 *Cassiope tetragona* heath (from here on referred to as heath), in September 2012. Mean  
150 annual air temperature is around -10 °C and annual precipitation is 150-200 mm (Elberling et  
151 al. 2008). The area lies inside the zone of continuous permafrost with soil temperatures at 5  
152 cm depth below -18 °C four months a year and above 0 °C for about four months a year  
153 (Elberling et al. 2008).

154

155 The vegetation in the heath is composed of *Cassiope tetragona* (L.) D. Don with some *Salix*  
156 *arctica* Pall., *Poa alpina* L., *Luzula confusa* Lindeb., *Cetraria islandica* Ach., *Polytrichum*  
157 *spp.* and *Dicranum spp.* (a full vegetation inventory can be found in Lindwall et al. (2015).

158 The heath is located on sandy moraine, where four soil horizons have earlier been identified  
159 (Elberling et al. 2004; Elberling et al. 2008): an A horizon between 0 and 5 cm, a B/C horizon  
160 between 5 and 17 cm, a relict Holocene Climate Optimum A<sub>b</sub> horizon buried between 17 and  
161 22 cm, and a C horizon from 22 cm and down to the permafrost below the active layer  
162 maximum depth (approx. 65 cm).

163

164 The fen was dominated by *Eriophorum scheuchzeri* Hoppe and *Carex spp.* with some  
165 sporadic *L. confusa*, *S. arctica*, *Ranunculus spp.*, *Bistorta vivipara* (L.) Delarbre, *C. islandica*,  
166 *Polytrichum spp.*, *Dicranum spp.*, and *Hylocomium spp.* The fen is situated in a depression  
167 and affected by a fast deposition of sediment, caused by an input of organic material  
168 transported with meltwater. This site has earlier been classified, based on remote sensing data,  
169 as Grassland with water saturation of 60-100% (Elberling et al. 2008).

170

### 171 **Soil sampling**

172 Soil sampling was conducted in three soil pits (70x70 cm) per ecosystem type, and where the  
173 soil was divided into three different layers. At the heath site, the upper organic-rich soil (0 to  
174 approx. 7 cm depth), was sampled as A horizon. The second, silt dominated layer with  
175 organic patches (down to approx. 32 cm depth), was sampled as the B/C horizon avoiding  
176 sampling cryoturbated organic or relict A<sub>b</sub> horizon patches. The third, sandy layer down to the  
177 active layer maximum depth (approx. 65 cm), was sampled as C horizon. For the fen site,  
178 distinct soil layers were not easily detected, with more organic material throughout the full  
179 active layer, and where the top 0 to 5 cm was sampled as the A horizon. The second layer  
180 (down to approx. 25 cm depth) was sampled as a B horizon, while the remaining part of the  
181 active layer (down to approx. 57 cm) was sampled as the C horizon. Each soil layer was  
182 sampled four times per pit, with one sample from each wall of the pit, using a 4.5 cm diameter  
183 metal tube. The four samples were then homogenized on site forming one bulk sample per  
184 layer and soil pit. The pits were then left open for a few days to further melt the top part of the  
185 frozen soil and later the top 20-30 cm of the permafrost was sampled with a portable soil  
186 drilling machine, using a diamond drill bit (5.5 cm in diameter). Four cores were extracted  
187 from each pit, with an excavation depth of approx. 64 to 88 cm for the heath site and approx.  
188 59 to 78 cm for the fen site. Samples were kept and shipped frozen until analysis.

189

### 190 **Experimental set-up**

191 Experiments were performed on soil samples from the permafrost and the second layer of  
192 active soil (B/C for heath and B for fen). Soil samples from the A and C horizons were not  
193 available for the present study. The frozen soil cores were split into particles <1 cm<sup>3</sup> in a  
194 freezer room using a hammer and a metal mesh (8 mm mesh size). Permafrost soils were

195 divided into two sub-samples. One sub-sample was placed on 200 g fine quartz sand (particle  
196 size 0.2-0.3 mm) (Silhorko-Eurowater A/S, Skanderborg, Denmark) to drain the meltwater  
197 from the sample while the other sub-sample was incubated without sand. Before the  
198 experiment, the sand was heated at 120 °C for two hours, to remove contamination in the  
199 sand.

200  
201 The soil samples were incubated for a twelve-day period in 2015 to assess the release of  
202 BVOCs upon thaw. Frozen soil samples (fresh weight 30-100 g) were incubated at 2 °C in  
203 500 ml glass jars sealed by aluminum foil coated screw lids. The soil covered the entire  
204 bottom of the jar (diameter 8 cm) and had a depth of 2-3 cm. The glass jars and lids had been  
205 carefully cleaned and heated at 120 °C for two hours prior to the experiment. After 48 h, the  
206 accumulated release of BVOCs was sampled, and the headspace was sealed again to allow for  
207 the accumulation of gases for another 48 h, followed by sampling on day 4. Thereafter, the  
208 incubation temperature was raised to 10 °C, followed by a BVOC sampling on day 8, and  
209 then further raised to a temperature of 20 °C. The final BVOC sampling was done on day 12.  
210 The measurements on day 8 and 12 were performed to estimate the BVOC emission rates  
211 rather than the accumulation of compounds, and therefore the jars were ventilated for 10  
212 minutes with an inflow rate of 1000 ml min<sup>-1</sup>, prior to sampling. This was long enough to  
213 reach the steady-state as tested by online measurements with proton transfer reaction – time of  
214 flight – mass spectrometry in Kramshøj et al. (2018).

215 In the remaining part of the manuscript we will refer to the soil BVOC accumulation  
216 measurements after 48 and 96 h as “thawed soils”, and the soil BVOC emission rate  
217 measurements at day 8 and 12 h as “warmed soils”.

218 Empty jars with and without sand were used as blanks and sampled following the same  
219 practice as the soil samples. At the end of the experiment, gravimetric soil water content and

220 soil organic matter (SOM) were determined based on the water loss after drying at 70 °C for  
221 24 h and by loss on ignition at 550 °C for 6 h, respectively.

222

### 223 **Measurements of BVOC emission**

224 BVOC emission from soil samples was sampled using a flow through system. Air was  
225 circulated through the jar by battery-operated pumps (12 V; Rietschle Thomas, Puchheim,  
226 Germany) via Teflon tubes attached to stainless steel ball valves (Roykon, Fredericia,  
227 Denmark) mounted on the jar lids. In- and outflow was set to 200 ml min<sup>-1</sup>. The flow rates  
228 were regulated using mass flow sensors (D6F-P0010A1, Omron, Kyoto, Japan), and  
229 additionally calibrated using mini BUCK Calibrator M-5 before and after each measurement.  
230 The incoming air was purified by a charcoal filter to remove particles and VOCs present in  
231 ambient air, and by a copper tubing coated with potassium iodide to remove ozone (Ortega et  
232 al. 2008). It should be noted that the use of clean inlet air can have artificially increased  
233 BVOC emissions by increasing the diffusion rate from the soil pores to the headspace air.  
234 Air was pulled out of the jars through stainless steel adsorbent cartridges containing 150±1.5  
235 mg Tenax TA and 200±2.0 mg Carbograph 1TD (Markes International Limited, Llantrisant,  
236 United Kingdom). Following the 60 min sampling, the cartridges were sealed with Teflon-  
237 coated brass caps and stored at 2 °C until analysis. The used adsorbent cartridges retain  
238 hydrocarbons in the range of C<sub>5</sub>–C<sub>25</sub> as well as some smaller compounds containing  
239 heteroatoms, and the detection limit is around 1 ng depending on the compound.

240

### 241 **Analysis of BVOCs**

242 Analysis, identification and quantification of BVOCs sampled in the adsorbent tubes were  
243 performed according to Kramshøj et al. (2016). Briefly, the BVOC samples were analyzed by  
244 a gas chromatograph–mass spectrometer after thermal desorption and the compounds were

245 separated in an HP-5 capillary column. Compounds were identified using pure standards (See  
246 Table S1 for a list of compounds) or based on mass spectra similarity in the NIST 8.0 mass  
247 spectral data library, while quantification was performed with pure standards. When a pure  
248 standard was not available,  $\alpha$ -pinene was used for monoterpenes, humulene was used for  
249 sesquiterpenes and toluene was used to quantify other compounds.

250 In the blank measurements, most of the compounds had emission rates below 0.5 ng glass jar<sup>-1</sup>  
251 h<sup>-1</sup>. The BVOC concentrations in blank samples were subtracted from those in the soil  
252 samples. Further, for a compound to be included as present in a given sample, the  
253 concentration in the sample had to be twice the average of the blanks measured at the same  
254 time. Compounds were put in following groups: acids and esters, alcohols, aldehydes,  
255 alkanes, alkenes, benzenoids, ketones, compounds containing sulfur or nitrogen and  
256 terpenoids.

257

### 258 **Soil chemistry and microbial biomass**

259 The frozen soil samples were at placed 5 °C the day before the chemical and microbial  
260 analyses. Stones, roots and undecomposed plant parts were removed from the soil samples by  
261 hand and pH was determined from soil extracts using a pH-meter. Thereafter, the samples  
262 were divided into two subsamples each analyzed as described below.

263

264 For microbial biomass estimation, 5 or 10 g fresh weight soil was fumigated with ethanol-free  
265 chloroform under low pressure for 24 h to lyse microbes. After fumigation, the analytes of  
266 interest were extracted in 25 (for 5 g soil samples) or 50 (for 10 g soil samples) ml deionized  
267 water on a rotary shaker for 1 h. Another non-fumigated subsample was extracted in a similar  
268 way. The extracts were filtered through Whatman GF-D glass microfiber filters (Whatman  
269 Ltd., Maidstone, UK). The extracts were and further analyzed for dissolved organic C (DOC)

270 with a TOC-L total organic carbon analyzer (Shimadzu, Kyoto, Japan). Inorganic nitrogen  
271 ( $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N) and total dissolved N (TDN) were measured using an FIA STAR 5000  
272 flow injection analyzer (FOSS Tecator, Höganäs, Sweden). Microbial biomass C was  
273 calculated as the difference in DOC between fumigated and non-fumigated extracts. A  
274 conversion factor ( $k_{\text{EC}}$ ) of 0.45 was used to compensate for incomplete extractability  
275 (Joergensen 1996).

276

### 277 **Q<sub>10</sub>-value for BVOC emission**

278 Q<sub>10</sub> was calculated using the following formula:

$$Q_{10} = \frac{R_2}{R_1} \frac{10^\circ\text{C}}{t_2 - t_1}$$

279 where  $R$  is the average BVOC emission rate and  $t$  is the temperature in Celsius and where  $t_1$   
280 and  $t_2$  indicate the higher and lower incubation temperature, respectively.

281

### 282 **Statistical analyses**

283 The BVOC release and emission profiles were analyzed using multivariate data analyses in  
284 SIMCA (Umetrics, Umeå, Sweden). Principal component analyses (PCA) were performed on  
285 the release and emission data in order to assess grouping of the samples according to  
286 ecosystem type, soil horizon, temperature and drainage conditions. Compounds appearing in  
287 less than 70% of the samples were not included in the analyses. Data were mean centered and  
288 scaled to unit-variance to let all compounds have equal importance. Outliers, identified based  
289 on Residual- and Hotelling's T-squared values, and variables not contributing to the  
290 explanatory power of the PCA model were removed.

291

292 In order to investigate whether the emission profiles correlate with soil water content, soil  
293 organic matter (SOM), and pH, one-component partial least squares regression (PLS) models

294 were computed with the above mentioned factors as Y-variable and the emission rates of  
295 individual BVOCs as X-variables. Samples measured at 10 °C were excluded from the  
296 analyses, as values of SOM, pH and soil water content were identical for 10 °C and 20 °C  
297 measurements. For the PLS model with pH as Y-variable, non-drained permafrost soils were  
298 excluded as pH data was missing for these samples. Data were preprocessed similar to the  
299 PCAs.

300

301 The data on BVOC groups was tested in IBM SPSS Statistics (Version 22.0, IBM Corp., New  
302 York City, United States). The effects of soil horizon, ecosystem type and drainage conditions  
303 on the release of BVOCs were tested in General Linear Model Repeated Measures Analysis  
304 of Variance (RM-ANOVA) with thaw period and ecosystem type (fen; heath) as a within-  
305 subjects factors and soil horizon/drainage (B horizon soil; drained permafrost soil; non-  
306 drained permafrost soil) as a between-subjects factor. RM-ANOVA was also used to test for  
307 the effects of ecosystem type, soil horizon, drainage conditions and temperature (10 °C; 20  
308 °C) on BVOC emission rates. Temperature was a within-subjects factor and ecosystem type  
309 and soil horizon/drainage between-subjects factors. When a significant interaction was found,  
310 additional testing of the variables was performed separately, in order to analyze the nature of  
311 the effect. Due to the multiple tests performed on the nine BVOC groups the significance  
312 level was adjusted with the Sidák correction to an  $\alpha$  of 0.0051 in these analyses. A Tukey's  
313 *post hoc* test was used for pairwise comparisons of the three factor categories of soil  
314 horizon/drainage. Differences in principal component scores between soil horizon/drainage  
315 groups were tested in Univariate Analysis of Variance and with Dunnett C as post hoc test.

## 316 Results

### 317 Release of BVOCs from thawed soils

318 In the thawed soils, the largest BVOC release came from the drained fen permafrost soils and  
319 amounted to approximately 80 ng BVOC g<sup>-1</sup> dry weight soil, which was more than three times  
320 as much as the release from any of the other samples (Fig. 1a). The release of alcohols,  
321 ketones and total BVOCs was 13, three and seven times higher in fen than in heath soils,  
322 respectively, as averaged across the soil horizon and drainage treatment (Fig. 1a and  
323 Supplementary Fig. 1). Overall, the total sum of BVOCs released was 10 and 13 times higher  
324 when the meltwater was drained from the soil as compared to the non-drained soils for fen  
325 and heath soils, respectively (Fig. 1a; Supplementary Table S1). Drained permafrost released  
326 more BVOCs than the B horizon in the fen ( $P=0.001$ ), while there was no difference in the  
327 heath (Fig. 1a).

328

### 329 *Composition of compounds released upon thaw*

330 During the incubation period of 96 h, a total of 144 and 153 different compounds were  
331 released from the thawed fen and heath soil samples, respectively. Pentane, 2-butanone,  
332 toluene, p-cymene and p-xylene were the most significant components (Supplementary Table  
333 S2). Across all soils, alkanes (dominated by pentane) and benzenoids (dominated by toluene  
334 and p-xylene) were the most abundant BVOC groups, contributing with 39% and 30% of the  
335 total release, respectively (Fig. 1b). Benzenoids accounted for 59% of the total BVOC release  
336 in the B horizon soils, and 19% in the permafrost soils averaged across ecosystem types. In  
337 contrast, the contribution of alkanes was 44% for permafrost soil and 27% for the B horizon  
338 soil (Fig. 1b). Also, alcohols (dominated by 2-ethyl-1-hexanol), aldehydes (dominated by  
339 several compounds) and ketones (dominated by several compounds) were released relatively  
340 more from thawed permafrost soils compared to thawed B horizon soils (Fig. 1b). The release



341 of alkenes was associated with the drained permafrost soil in general, and the compounds  
342 containing sulfur or nitrogen were associated with the fen permafrost soils. The principal  
343 component analysis (PCA) performed on the individual compounds released showed that  
344 samples grouped according to soil horizon/drainage. For PC1 scores, all three groups (B  
345 horizon; drained permafrost; non-drained permafrost) were statistically significantly different  
346 from each other ( $P<0.05$ ), and for PC2, B horizon was statistically significantly different from  
347 both drained and non-drained permafrost soils (Fig. 2a).

348

### 349 **Emission rates in warmed soils**

350 In the warmed soils, the total BVOC emission rate was similar in fen and heath soils.  
351 However, the effect of soil horizon and drainage conditions varied between the two ecosystem  
352 types (Fig. 1c; Table 1). In the heath, there was no significant difference in emission rates  
353 between soil horizons and drainage conditions, while the contrary was true in the fen. Here,  
354 the average BVOC emission rate from drained permafrost was ten times higher than the  
355 emission from B horizon soils and six times higher than that from the non-drained permafrost  
356 soils averaged across temperature (Fig. 1c).

357

### 358 *Temperature dependence of emissions*

359 The emission rate was significantly higher at 20 °C than 10 °C in all groups except for four  
360 groups (alcohols, compounds containing sulfur or nitrogen, terpenoids and aldehydes) (Fig.  
361 1c; Supplementary Fig. 1). Across all soils, this corresponded to a  $Q_{10}$  value of 2.5 for total  
362 BVOCs, however emission response to temperature varied between BVOC groups. Acids and  
363 esters responded the most to temperature having a  $Q_{10}$  value of 8.3, followed by alkanes with  
364 a value of 4.3, while aldehydes, terpenoids, ketones, benzenoids, and sulfur and nitrogen  
365 compounds all had  $Q_{10}$  values below 2 (Supplementary Fig. 1).

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Emission response to temperature varied between BVOC groups. Acids and esters responded the most to temperature having a  $Q_{10}$  value of 8.3, followed by alkanes with a value of 4.3, while aldehydes, terpenoids, ketones, benzenoids, and sulfur and nitrogen compounds all had  $Q_{10}$  values below 2 (Supplementary Fig. 1).

#### *Compound composition of BVOC emissions*

In total, 159 compounds were emitted from the heath soils and 161 from the fen soils, with alkanes (dominated by 3-methyl-hexane and 2,3-dimethyl-pentane) and benzenoids (dominated by benzene and benzaldehyde) accounting for 39% and 30% of the total emission rate, respectively (Fig. 1d; Supplementary Table S3). The most emitted compounds were 2-ethyl-1-hexanol, 3-methyl-hexane, 2-butanone and 2,3-dimethyl-pentane. Alkanes especially dominated the emission from the heath soils, accounting for 65% of the total emission, while only accounting for 13% of the fen soil emission (Fig. 1d).

Benzenoids accounted for an average of 57% of the B horizon and 17% of the permafrost soil emissions (Fig. 1d; Fig. 2). In both ecosystem types, the relative emissions of acids and esters (dominated by methyl carbonate), aldehydes (dominated by hexanal), alcohols (dominated by 2-ethyl-1-hexanol) and ketones (dominated by 2-butanone) were higher in permafrost soils than in the B horizon soils (Fig. 1d). Emission of alkenes was together with many alcohols, aldehydes and ketones associated with the drained permafrost soil (Fig. 1d; Fig. 2). The PCA performed on the emission rates of individual BVOCs showed that samples grouped according to the soil horizon/drainage. The first principal component (PC1) separated the drained permafrost soils from non-drained permafrost soil and the B horizon soil ( $P < 0.05$ ), while the PC2 separated the non-drained permafrost soils from drained permafrost soil and B

391 horizon soil ( $P < 0.05$ ) (Fig. 2c). In addition, the PCA suggested that B horizon soil emissions  
392 were dominated by benzenoids, while alcohols and ketones were relatively more abundant in  
393 the drained permafrost (Fig. 2).

394

#### 395 **Soil nutrients, pH, water- and organic matter content**

396 Soil water content was twice as high in the permafrost compared to the B horizon (Table 2),  
397 and the SOM content of the soils was 2.3-8.5%. Averaged across the soil types, the water  
398 content and SOM were twice as high in the fen compared to the heath. The pH was similar in  
399 the fen and heath B horizon soil (Table 2). In the heath, the pH in the permafrost was higher  
400 compared to the B horizon soils. The heath soils contained higher amounts of dissolved  
401 phosphorus compared to the fen (Table 3). Dissolved organic carbon content was higher in  
402 the permafrost than in the B horizon while total dissolved nitrogen was higher in the B  
403 horizon compared to the permafrost soil. Microbial carbon,  $\text{NO}_3\text{-N}$  and  $\text{NH}_4\text{-N}$   
404 concentrations showed no clear pattern.

405 The PLS regression analyses performed with soil water content, SOM or pH as Y-variable  
406 revealed that these variables strongly correlated with the emission profile, i.e. the composition  
407 of the compound mixture released was a fingerprint for the soil sample and reflected its water  
408 content, SOM and pH.  $R^2$  in the observed vs. predicted plots was 0.90 for water content, 0.89  
409 for SOM and 0.84 for pH (Fig. 3). Root Mean Squared Error of Estimation, representing one  
410 standard deviation in the metric of the Y variable, was 1.17 for SOM, 4.80 for soil water  
411 content and 0.29 for pH.

## 412 Discussion

413 We found that the composition of BVOCs emitted depended on both soil horizon and  
414 ecosystem type. Allowing drainage of the meltwater upon permafrost thaw changed the  
415 compound composition in both heath and fen soils and increased the total emission  
416 significantly from fen permafrost soils. The emissions were temperature-dependent, and pH,  
417 soil water content and SOM correlated well with the BVOC emission profile. The BVOC  
418 emission rate from the warmed soils was in the same range as the emission rate measured for  
419 boreal peat incubations (Faubert et al. 2010; Faubert 2011).

420 In the thawed soils, we observed the release of a small pulse of BVOCs during the first 96 h  
421 following thaw. Both the magnitude and the compound composition differed between  
422 ecosystem type, soil horizon and drainage conditions. This initial release could both be a  
423 result of trapped gases escaping the permafrost soil as it thaws, but also originate from a new  
424 production of compounds by microbes active shortly after the thaw.

425

### 426 *BVOC release from thawed soils*

427 In the thawed fen soils, the release of BVOCs from drained permafrost exceeded that from the  
428 B horizon of the active layer, supporting our first hypothesis. We propose that such a  
429 difference may be due to a longer build-up period of gases in the permafrost soils since soil  
430 microbes are active even below freezing (Panikov et al. 2006). In the heath soil, however,  
431 there was no difference between the release of BVOCs in B horizon and drained permafrost  
432 soils. A possible explanation is that B horizon soils in the heath contained more SOM than  
433 permafrost soils, SOM being an important precursor for BVOCs (Leff and Fierer 2008). The  
434 release of BVOCs upon thaw from non-drained permafrost soils was lower than the release  
435 from the B horizon and drained permafrost for both heath and fen soils. This is most likely  
436 caused by slow diffusion in the water-covered non-drained permafrost since diffusion rates in

437 water are around 10,000 times slower than the diffusion rates in air (Scharzenbach et al.  
438 1993). We conclude that the initial release of BVOCs from thawed permafrost depends on the  
439 carbon content of the permafrost and the fate of meltwater in this permanently frozen soil.

440

441 *Temperature, soil horizon and ecosystem type dependence of BVOC emissions from warmed*  
442 *soils*

443 In the warmed soils, the emissions of all individual BVOC groups, except aldehydes, as well  
444 as the sum of all groups increased with temperature, which is in strong agreement with our  
445 second hypothesis. This finding is in accordance with other studies (Asensio et al. 2007;  
446 Faubert et al. 2011) and was well expected as temperature impacts BVOC emission through  
447 several mechanisms including microbial activity and compound volatility. The  $Q_{10}$  for the  
448 total BVOC emission was 2.5, which is normal for biological processes (Niinemets 2004),  
449 and in line with  $Q_{10}$  estimates of  $CO_2$  soil production from the same sites (Elberling and  
450 Brandt 2003) but lower than the  $Q_{10}$  for plant BVOC emission usually being around 3-6  
451 (Peñuelas and Staudt 2010). In particular, acids, esters and alkanes responded strongly to an  
452 increase in temperature, while aldehydes, terpenoids and ketones were less temperature  
453 sensitive. Since we measured the net emission and not the gross production of the compounds,  
454 we cannot say if this difference in temperature response is due to different changes in BVOC  
455 production, microbial consumption or a combination of these two opposing processes,  
456 however, it is clear that temperature has large impact on BVOC emission.

457

458 The PCA performed on the emission of individual BVOCs from warmed soils, show that  
459 distinct BVOC emission profiles were emitted from the B horizon and the permafrost soil. For  
460 example, benzenoids accounted for 57% of the total BVOC emission from the B horizon, as  
461 compared to 17% in the permafrost soil that had a more diverse emission profile, in which

462 ketones were well represented. In general, bacteria emit more ketones than fungi that on the  
463 other hand emit more benzenoids (Peñuelas et al. 2014). Hence, it is possible that differences  
464 in microbial community composition will cause emission profiles to vary, and that fungal  
465 emissions were more important in the B horizon compared to permafrost in our study. Arctic  
466 mineral and permafrost soils have previously been shown to house different microbial  
467 communities, and while bacteria to fungal ratio is higher in permafrost soils compared to  
468 Arctic mineral soils (Kramshøj et al. 2018), the bacteria to fungal ratio in Arctic active layer  
469 tundra soil is comparable to that of a temperate beech soil (Albers et al. 2018). Even though  
470 microbial community composition in permafrost soils changes rapidly following thaw  
471 (Mackelprang et al. 2011; Wilhelm et al. 2011; Gittel et al. 2014a; Gittel et al. 2014b), it  
472 remains distinct from that in the active layer (Mackelprang et al. 2011). BVOC emissions  
473 from soils not containing living plant roots primarily originate from microbial activity (Insam  
474 and Seewald 2010; Peñuelas et al. 2014). An example of this microbial dependence of BVOC  
475 production is the relatively high 1-butanol emission in the permafrost soils, which fits the  
476 findings of Lipson et al. (2013), who investigated an Alaskan soil horizon metagenome, and  
477 found high numbers of genes (members of the genus *Clostridia*) involved in a fermentative  
478 metabolic pathway in the upper permafrost layer, producing butanol. Thus, the discrepancy in  
479 emission profiles between the B horizon and permafrost soils, as well as the temperature  
480 sensitivity in our study, suggests a strong microbial control of BVOC release from Arctic  
481 soils.

482

483 The total BVOC emission from the warmed fen and heath soils was of the same magnitude,  
484 while the compound compositions differed. Again, this may reflect the importance of the  
485 microbial communities, which have been found to differ significantly between wet sedge and  
486 dry heath vegetation (Chu et al. 2011). Key parameters for shaping the soil microbial

487 communities are the quality and quantity of the organic input to the soil (Blagodatskaya and  
488 Kuzyakov 2008). One could speculate that especially the quality of the organic matter, which  
489 would differ between the two ecosystems, could in itself influence the emission profile. The  
490 partial least squares regression models could well predict the soil water content, SOM and pH  
491 of a soil sample based on its BVOC emission profile. This shows that BVOC emissions are  
492 likely related to one or more of these soil variables or another inter-correlated variable that  
493 was not measured. Since soil water content and SOM were twice as high in the fen compared  
494 to the heath this is likely also part of the explanation for the different emission profiles. A  
495 warmer climate is predicted to alter a range of soil characteristics in the Arctic, such as  
496 moisture (IPCC, 2013) and SOM (Cornelissen et al. 2007; Feng et al. 2008), and this could  
497 lead to a change in compound composition in the future. Relatively more ketones and  
498 alcohols were emitted from the fen soils, while alkanes were associated with emission from  
499 heath soils. Several ketones and alcohols are products of anaerobic fermentation processes,  
500 possibly explaining their higher emission from the fen soils, holding more anoxic microsites.

501

#### 502 *Effect of meltwater drainage on BVOC emission upon permafrost thaw*

503 In the fen, total BVOC emission rates from drained permafrost soils were nine times higher  
504 than those from non-drained permafrost soils, contrasting with our third hypothesis. However,  
505 drainage had no significant impact on emissions from warmed permafrost in the heath,  
506 possibly explained by the fact that permafrost soils in the heath only contained half as much  
507 water as the fen permafrost soils. Contrary to our findings, Kramshøj et al. (2018) found a  
508 positive correlation between BVOCs release from thawing permafrost soils and soil water  
509 content, however in that study primarily low weight BVOCs such as ethanol and methanol  
510 were targeted. Faubert et al. (2010) used a microcosm incubation experiment to study the  
511 BVOC emission response to water table drawdown in waterlogged boreal peatland soils with

512 intact and cut-off vegetation and found – also in contrast to our findings – that drainage  
513 decreased emissions. The authors argued that this was caused by a decrease in fermentation  
514 processes and associated BVOC release in the more oxic soil (Insam and Seewald 2010), and  
515 by increased microbial BVOC degradation rates (Faubert et al. 2010). Our divergent results  
516 could be explained by differences in the height of the water table, as diffusion of hydrophobic  
517 compounds in water is very slow compared to diffusion in air (Scharzenbach et al. 1993). The  
518 height of the water table is therefore critical for diffusion rates to the atmosphere. How well  
519 the meltwater is drained from the soil following a permafrost thaw event will influence the  
520 soil BVOC emission rates in the short term. The BVOCs retained in the waterlogged soil  
521 could either undergo microbial degradation or be released at a later stage.

522

523 Alkenes and terpenoids were emitted relatively more in the drained permafrost soils compared  
524 to the non-drained permafrost soils. This could be related to higher bacterial activity in the  
525 drained soils, as these compound groups are primarily emitted by bacteria (Peñuelas et al.  
526 2014). Faubert et al. (2011) studied emission from drained ombrotrophic peat soils, which had  
527 previously been incubated either with a normal water table or with a 20 cm water table  
528 drawdown. Similar to our study, they found relatively higher terpenoid emissions in the drier  
529 soils exposed to water table drawdown compared to the wetter soils with normal water table.  
530 This is well in agreement with the fact that secondary metabolites such as terpenoids often  
531 dominate the BVOC emission profile under aerobic conditions, while BVOCs associated with  
532 fermentation processes dominate in anaerobic conditions (Insam and Seewald 2010).

533

534 Opposed to surface gas fluxes, subsurface gas production cannot be easily measured in the  
535 field, and therefore needs to be determined by indirect methods such as soil incubations. Soil  
536 incubation experiments have proved to be a reliable method for estimating soil CO<sub>2</sub> and CH<sub>4</sub>



537 production in the field (Hodgkins et al. 2015), and the determination of soil CO<sub>2</sub> and CH<sub>4</sub>  
538 emission using incubations is a widely accepted method, providing data for emission models  
539 (Schädel et al. 2014; Schuur et al. 2015). So far, however, no one has tested if the incubation  
540 method can provide realistic estimates for subsurface soil BVOC emissions. Incubation of  
541 soil causes alterations to *in situ* conditions, including isolation from the surrounding soil  
542 environment (and vegetation), shifts in the microbial community due to introduction and  
543 extinction of species, exposure to oxygen and changed soil water content. The emission  
544 magnitude observed in this study could therefore differ significantly from what occurs in  
545 nature, and direct extrapolation of the results is not advisable. Nonetheless, since near-surface  
546 permafrost soils (0-3 m) that contain an estimated 1035 Pg carbon, are projected to decrease  
547 by 60% (i.e. thaw) by 2100, it is likely that the permafrost soil BVOC emission rates  
548 discovered in this study will have consequences. Based on the average BVOC emission rate  
549 from warmed permafrost soils at 10 °C (approximately 20 ng g<sup>-1</sup> h<sup>-1</sup>) observed in this study,  
550 21 billion tons of BVOCs would be released from thawing permafrost soil by the end of the  
551 century assuming the above mentioned estimations hold. When the permafrost is overlain by  
552 aerobic active layer soil the majority of these compounds will be decomposed by microbes  
553 (Kramshøj et al. 2018), but it is unknown if this is also the case under waterlogged conditions.  
554 Furthermore, in non-vegetated areas of the Arctic, where there is no constant flow of exudates  
555 from plant roots to the microbes (Brimecombe et al. 2007), it is possible that a large release of  
556 BVOCs from the permafrost soil could be an important carbon source for the microbial  
557 community. If so, permafrost soil released BVOCs could potentially have a positive priming  
558 effect on mineralization rates, supporting a positive feedback loop between permafrost  
559 thawing, greenhouse gas release and global warming (IPCC 2013).  
560

561 To conclude, the results from this study suggest that meltwater drainage conditions can have a  
562 large impact on the magnitude and composition of BVOC emission following a permafrost  
563 soil thaw event in the short term. We hypothesize that three scenarios are likely to play out  
564 when permafrost soils thaw: 1) High BVOC emissions can be expected from partly drained  
565 soils, which will facilitate anaerobic fermentation processes that produce BVOCs but still  
566 keep microbial BVOC degradation to a minimum. The partly drained soil will also have a  
567 water table low enough, allowing diffusion to the atmosphere. 2) Well drained soils that are  
568 mostly oxic will have the second highest emission rates, likely having both high microbial  
569 BVOC production and degradation. 3) Waterlogged soils with a water table above the soil  
570 surface could have the lowest emission rates, if BVOCs detained in the water column are  
571 degraded before evaporating from the water surface. In order to fully comprehend how  
572 drainage conditions in the thawing Arctic permafrost impact BVOC emissions it is necessary  
573 to conduct studies that can separate the processes producing and degrading BVOCs under a  
574 variety of oxygen availabilities. Further, the process understanding should be validated with  
575 field data collected in situ.

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589

590 **Author contributions**

591 MK, RR, MB, RGB and CA designed the experiment. MB and FL sampled the soil. MK  
592 performed the laboratory experiment. SS performed the soil analyses. MK, RR and CA wrote  
593 the manuscript with contributions from all authors.

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784 **Table 1 | Effects of temperature, soil horizon/drainage and ecosystem on emissions from warmed soils.** *P*-values of  
785 main effects and interactions for the repeated measures analysis of variance (ANOVA) on emission rate of BVOC groups.  
786 Only interactions with *P*-values < 0.05 are shown. The significance level was set to *P*<0.0051 (Bonferroni correction) and  
787 significant *P*-values appear in bold. Temperature (10 °C; 20 °C), soil horizon/drainage (B horizon; drained permafrost; non-  
788 drained permafrost), ecosystem (heath; fen), S/N-compounds=sulfur or nitrogen containing compounds.

BVOC group	Temperature	Soil horizon/ drainage	Ecosystem	Temperature*Soil horizon/drainage	Ecosystem*Soil horizon/drainage
Acids and esters	<b>0.001</b>	<b>0.001</b>	0.148	<b>0.005</b>	0.386
Alcohols	0.024	0.028	0.023	0.151	0.075
Aldehydes	0.160	0.066	0.139	0.008	0.304
Alkanes	<b>0.003</b>	<b>0.002</b>	<b>0.003</b>	0.880	0.015
Alkenes	<b>0.001</b>	<b>0.004</b>	0.224	<b>0.002</b>	0.160
Benzenoids	<b>0.003</b>	0.009	0.546	0.508	0.224
Ketones	<b>0.001</b>	<b>0.001</b>	<b>0.004</b>	0.614	0.006
S/N-compounds	0.017	0.013	0.012	0.950	0.010
Terpenoids	0.013	<b>0.001</b>	0.034	0.362	0.200
Total BVOCs	<b>0.001</b>	<b>0.004</b>	0.858	0.498	0.035

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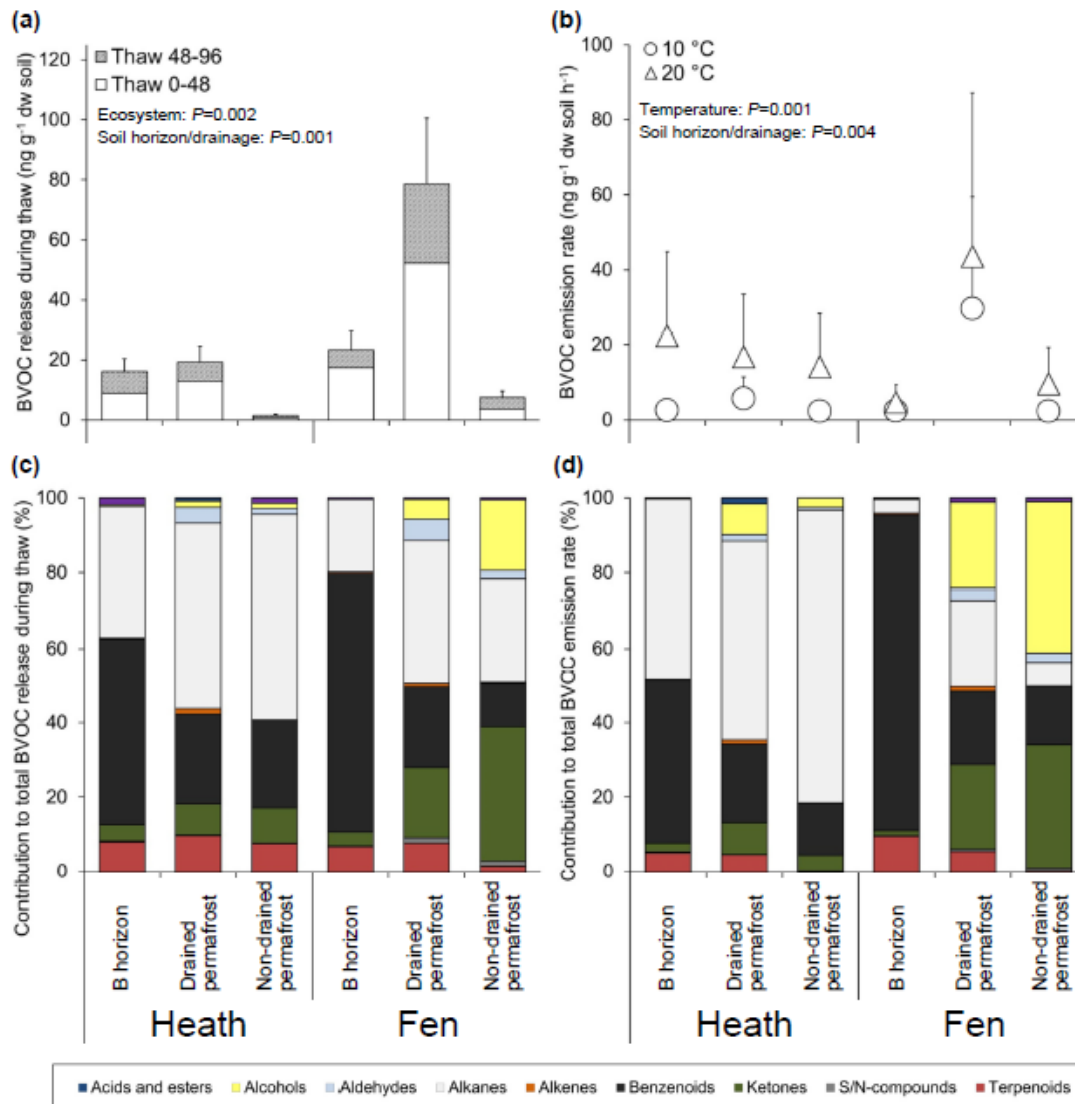
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803 **Table 2 | Soil parameters.** Measured soil parameters (n=3) in heath and fen bulk soils ( $\pm$  standard error of the mean).  
 804 SOM=soil organic matter; DOC=dissolved organic carbon; TDN=Total dissolved nitrogen. SOM=soil organic matter;  
 805 DOC=dissolved organic carbon; C<sub>mic</sub>=microbial carbon; TDN=Total dissolved nitrogen.

	<b>Heath</b>		<b>Fen</b>	
	<b>B horizon</b>	<b>Permafrost</b>	<b>B horizon</b>	<b>Permafrost</b>
Gravimetric soil water content (%)	12.6 $\pm$ 2.5	25.1 $\pm$ 0.7	29.4 $\pm$ 3.3	51.3 $\pm$ 3.0
SOM (%)	4.8 $\pm$ 1.0	2.3 $\pm$ 0.6	8.5 $\pm$ 1.2	7.5 $\pm$ 1.3
pH	6.2 $\pm$ 0.1	7.3 $\pm$ 0.1	5.8 $\pm$ 0.2	5.9 $\pm$ 0.3
DOC ( $\mu\text{g g}^{-1}$ dw soil)	90.3 $\pm$ 14.6	104.3 $\pm$ 31.1	60.9 $\pm$ 10.4	71.2 $\pm$ 5.0
C <sub>mic</sub> ( $\mu\text{g g}^{-1}$ dw soil)	69.0 $\pm$ 60.1	109.7 $\pm$ 6.2	144.8 $\pm$ 102.2	91.7 $\pm$ 85.3
NO <sub>3</sub> -N ( $\mu\text{g g}^{-1}$ dw soil)	1.0 $\pm$ 0.3	0.7 $\pm$ 0.3	0.7 $\pm$ 0.2	0.09 $\pm$ 0.02
NH <sub>4</sub> -N ( $\mu\text{g g}^{-1}$ dw soil)	1.0 $\pm$ 0.2	0.4 $\pm$ 0.04	0.8 $\pm$ 0.2	3.9 $\pm$ 1.3
TDN ( $\mu\text{g g}^{-1}$ dw soil)	14.8 $\pm$ 1.4	9.0 $\pm$ 1.3	17.0 $\pm$ 9.4	11.1 $\pm$ 0.9

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824 **Figure 1 | Biogenic volatile organic compound (BVOC) release from thawed and warmed heath and fen soils. a)**

825 Accumulated release of total BVOCs during 0-48 h and 48-96 h from thawed soils. Error bars are the standard error of the

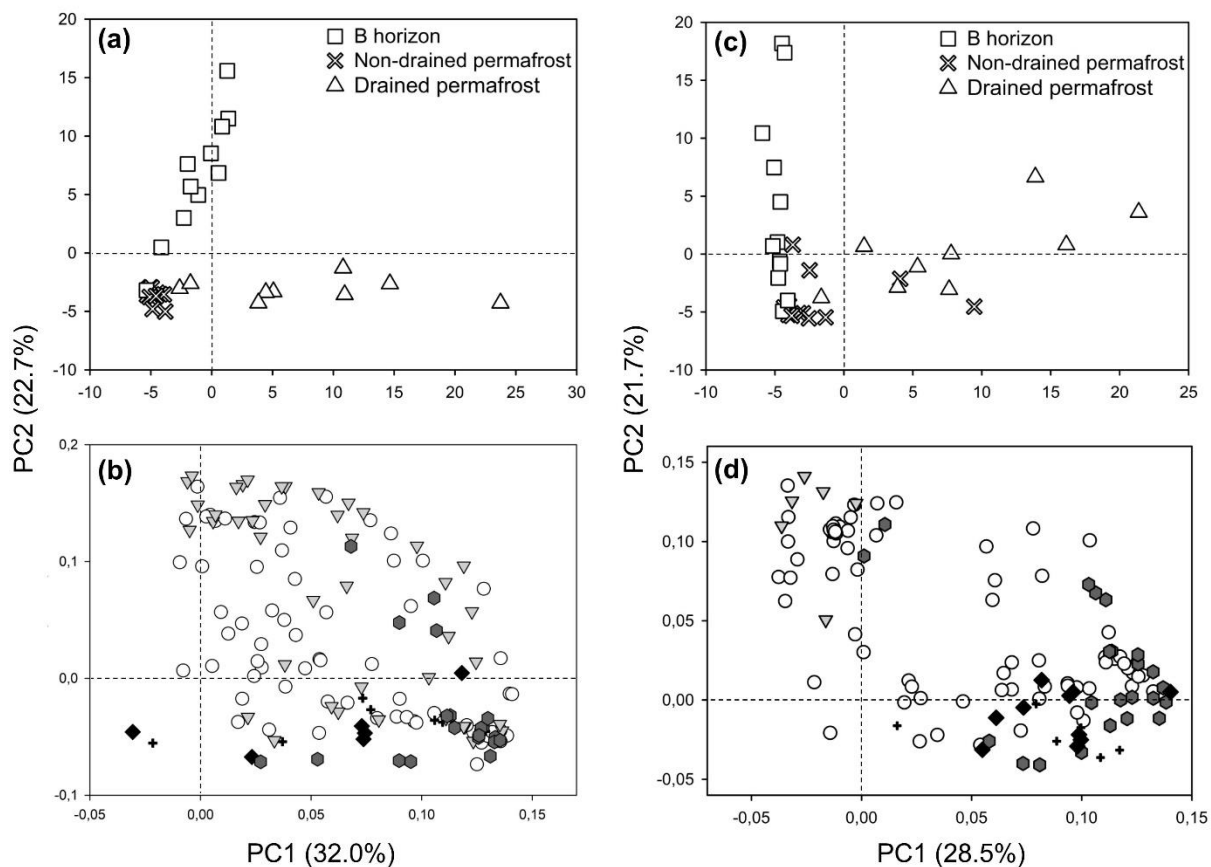
826 mean (SE) of the total accumulation during 0-96 h. b) Relative contribution of the BVOCs accumulated during 0-96 h

827 released from each group. c) Mean emission rate of total BVOCs at 10 °C and 20 °C (+ SE) from warmed soils. d) Relative

828 contribution of total BVOCs to emission (average of emission rate at 10 °C and 20 °C). All measurements were performed in

829 triplicates. Statistically significant  $P$ -values for the repeated measures analysis of variance (ANOVA) are shown in a and c.

830 dw=dry weight.



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832 **Figure 2 | Principal component analysis (PCA) on the release of individual compounds from thawed and warmed soils.**

833 a) Score plot of PCA on volatile release data from thawed, and b) the corresponding loading plot. c) Score plot of PCA on

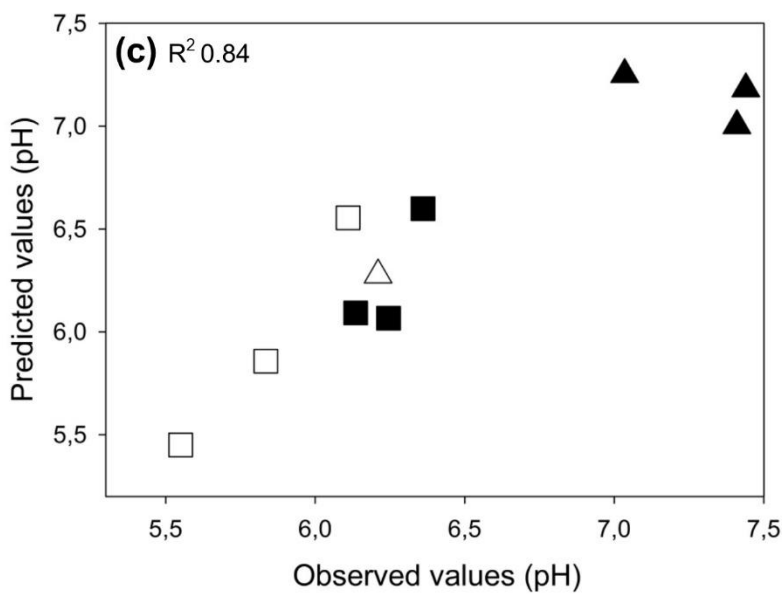
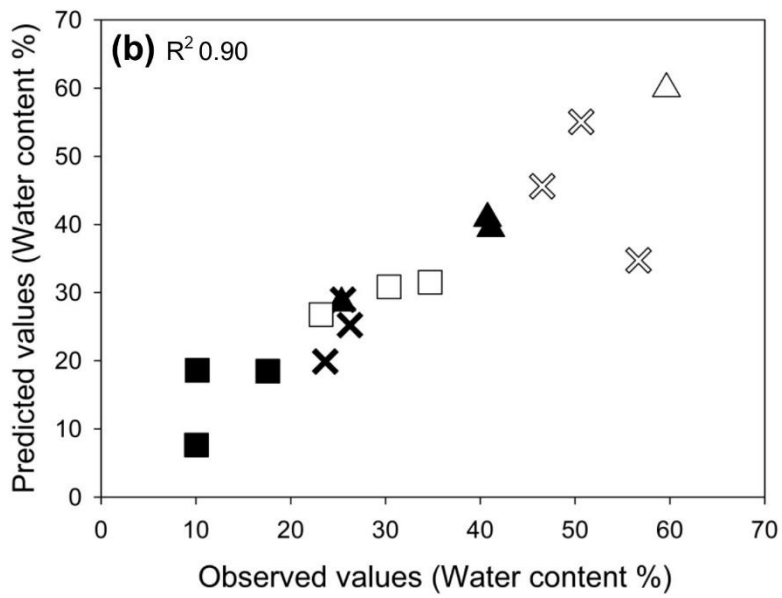
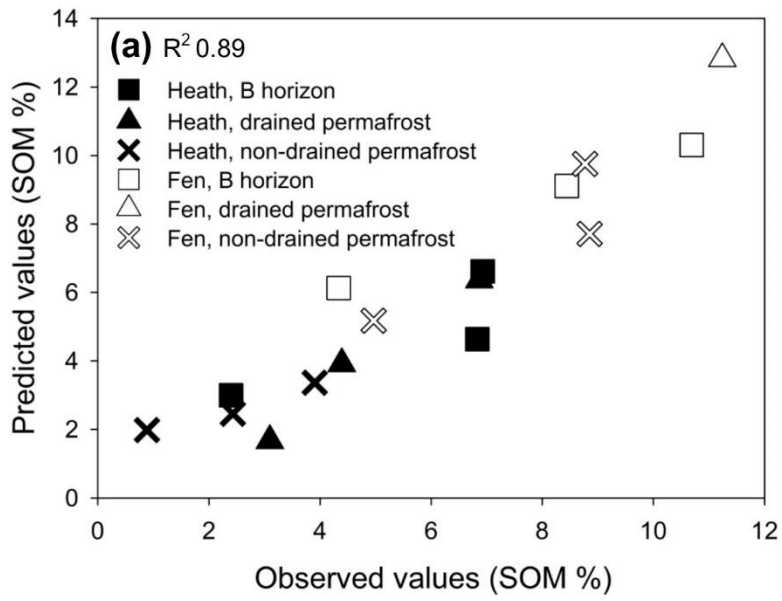
834 volatile emission rate data for warmed soils, and d) the corresponding loading plot. By comparing the coordinat distribution

835 of the compounds in the loading plots and the samples in the score plots, emission of specific compounds or compound

836 groups can be associated to certain soil horizons/drainage conditions. For b) and d): Alcohols=black diamonds,

837 benzenoids=light grey triangles, aldehydes=black plus signs, ketones=dark grey hexagons, other BVOCs=white circles.

838 Compound names for each loading variable are shown in Supplementary Table S4.



840 **Figure 3 | Emission profile as a fingerprint of soil characteristics.** Partial least squares (PLS) regression was used to  
841 assess how the emission profile of individual BVOCs released from warmed soil correlates with soil organic matter content  
842 (SOM), soil water content and pH. The observed vs. predicted plots of the 1-component PLS models are shown for a) SOM,  
843 b) soil water content and c) soil pH. Root Mean Squared Error of Estimation, representing one standard deviation in the  
844 metric of the Y variable, is 1.17 for SOM, 4.80 for water content and 0.29 for pH.

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