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

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Abstract

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

Introduction

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

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

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

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

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

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

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

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

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

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

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

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

Materials and methods

Site description

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

The vegetation in the heath is composed of *Cassiope tetragona* (L.) D. Don with some *Salix arctica* Pall., *Poa alpina* L., *Luzula confusa* Lindeb., *Cetraria islandica* Ach., *Polytrichum spp.* and *Dicranum spp.* (a full vegetation inventory can be found in Lindwall et al. (2015). The heath is located on sandy moraine, where four soil horizons have earlier been identified (Elberling et al. 2004; Elberling et al. 2008): an A horizon between 0 and 5 cm, a B/C horizon between 5 and 17 cm, a relict Holocene Climate Optimum A_b horizon buried between 17 and 22 cm, and a C horizon from 22 cm and down to the permafrost below the active layer maximum depth (approx. 65 cm).

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

Soil sampling

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

Experimental set-up

Experiments were performed on soil samples from the permafrost and the second layer of active soil (B/C for heath and B for fen). Soil samples from the A and C horizons were not available for the present study. The frozen soil cores were split into particles <1 cm^3 in a 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^{-1}, 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

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

Measurements of BVOC emission

BVOC emission from soil samples was sampled using a flow through system. Air was circulated through the jar by battery-operated pumps (12 V; Rietschle Thomas, Puchheim, Germany) via Teflon tubes attached to stainless steel ball valves (Roykon, Fredericia, Denmark) mounted on the jar lids. In- and outflow was set to 200 ml min^{-1}. The flow rates were regulated using mass flow sensors (D6F-P0010A1, Omron, Kyoto, Japan), and additionally calibrated using mini BUCK Calibrator M-5 before and after each measurement. The incoming air was purified by a charcoal filter to remove particles and VOCs present in ambient air, and by a copper tubing coated with potassium iodide to remove ozone (Ortega et al. 2008). It should be noted that the use of clean inlet air can have artificially increased BVOC emissions by increasing the diffusion rate from the soil pores to the headspace air. Air was pulled out of the jars through stainless steel adsorbent cartridges containing 150±1.5 mg Tenax TA and 200±2.0 mg Carbograph 1TD (Markes International Limited, Llantrisant, United Kingdom). Following the 60 min sampling, the cartridges were sealed with Teflon-coated brass caps and stored at 2 °C until analysis. The used adsorbent cartridges retain hydrocarbons in the range of C5–C25 as well as some smaller compounds containing heteroatoms, and the detection limit is around 1 ng depending on the compound.

Analysis of BVOCs

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

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

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

Soil chemistry and microbial biomass

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

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

with a TOC-L total organic carbon analyzer (Shimadzu, Kyoto, Japan). Inorganic nitrogen (NH_4^+-N and NO_3^--N) and total dissolved N (TDN) were measured using an FIA STAR 5000 flow injection analyzer (FOSS Tecator, Höganäs, Sweden). Microbial biomass C was calculated as the difference in DOC between fumigated and non-fumigated extracts. A conversion factor (k_{EC}) of 0.45 was used to compensate for incomplete extractability (Joergensen 1996).

Q_{10}-value for BVOC emission

Q_{10} was calculated using the following formula:

$$Q_{10} = \frac{R_2}{R_1}^{\frac{10\,°C}{t_2 - t_1}}$$

where R is the average BVOC emission rate and t is the temperature in Celsius and where $_1$ and $_2$ indicate the higher and lower incubation temperature, respectively.

Statistical analyses

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

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

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

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

Results

Release of BVOCs from thawed soils

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

Composition of compounds released upon thaw

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

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

Emission rates in warmed soils

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

Temperature dependence of emissions

The emission rate was significantly higher at 20 °C than 10 °C in all groups except for four groups (alcohols, compounds containing sulfur or nitrogen, terpenoids and aldehydes) (Fig. 1c; Supplementary Fig. 1). Across all soils, this corresponded to a Q_{10} value of 2.5 for total BVOCs, however 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).

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

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

Soil nutrients, pH, water- and organic matter content

Soil water content was twice as high in the permafrost compared to the B horizon (Table 2), and the SOM content of the soils was 2.3-8.5%. Averaged across the soil types, the water content and SOM were twice as high in the fen compared to the heath. The pH was similar in the fen and heath B horizon soil (Table 2). In the heath, the pH in the permafrost was higher compared to the B horizon soils. The heath soils contained higher amounts of dissolved phosphorus compared to the fen (Table 3). Dissolved organic carbon content was higher in the permafrost than in the B horizon while total dissolved nitrogen was higher in the B horizon compared to the permafrost soil. Microbial carbon, NO_3-N and NH_4-N concentrations showed no clear pattern.

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

Discussion

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

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

BVOC release from thawed soils

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

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

Effect of meltwater drainage on BVOC emission upon permafrost thaw

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

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

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

Opposed to surface gas fluxes, subsurface gas production cannot be easily measured in the field, and therefore needs to be determined by indirect methods such as soil incubations. Soil incubation experiments have proved to be a reliable method for estimating soil CO_2 and CH_4

production in the field (Hodgkins et al. 2015), and the determination of soil CO_2 and CH_4 emission using incubations is a widely accepted method, providing data for emission models (Schädel et al. 2014; Schuur et al. 2015). So far, however, no one has tested if the incubation method can provide realistic estimates for subsurface soil BVOC emissions. Incubation of soil causes alterations to *in situ* conditions, including isolation from the surrounding soil environment (and vegetation), shifts in the microbial community due to introduction and extinction of species, exposure to oxygen and changed soil water content. The emission magnitude observed in this study could therefore differ significantly from what occurs in nature, and direct extrapolation of the results is not advisable. Nonetheless, since near-surface permafrost soils (0-3 m) that contain an estimated 1035 Pg carbon, are projected to decrease by 60% (i.e. thaw) by 2100, it is likely that the permafrost soil BVOC emission rates discovered in this study will have consequences. Based on the average BVOC emission rate from warmed permafrost soils at 10 °C (approximately 20 ng g^{-1} h^{-1}) observed in this study, 21 billion tons of BVOCs would be released from thawing permafrost soil by the end of the century assuming the above mentioned estimations hold. When the permafrost is overlain by aerobic active layer soil the majority of these compounds will be decomposed by microbes (Kramshøj et al. 2018), but it is unknown if this is also the case under waterlogged conditions. Furthermore, in non-vegetated areas of the Arctic, where there is no constant flow of exudates from plant roots to the microbes (Brimecombe et al. 2007), it is possible that a large release of BVOCs from the permafrost soil could be an important carbon source for the microbial community. If so, permafrost soil released BVOCs could potentially have a positive priming effect on mineralization rates, supporting a positive feedback loop between permafrost thawing, greenhouse gas release and global warming (IPCC 2013).

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

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Author contributions

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

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Table 1 | Effects of temperature, soil horizon/drainage and ecosystem on emissions from warmed soils. *P*-values of main effects and interactions for the repeated measures analysis of variance (ANOVA) on emission rate of BVOC groups. Only interactions with *P*-values < 0.05 are shown. The significance level was set to *P*<0.0051 (Bonferroni correction) and significant *P*-values appear in bold. Temperature (10 °C; 20 °C), soil horizon/drainage (B horizon; drained permafrost; non-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	**0.001**	**0.001**	0.148	**0.005**	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	**0.003**	**0.002**	**0.003**	0.880	0.015
Alkenes	**0.001**	**0.004**	0.224	**0.002**	0.160
Benzenoids	**0.003**	0.009	0.546	0.508	0.224
Ketones	**0.001**	**0.001**	**0.004**	0.614	0.006
S/N-compounds	0.017	0.013	0.012	0.950	0.010
Terpenoids	0.013	**0.001**	0.034	0.362	0.200
Total BVOCs	**0.001**	**0.004**	0.858	0.498	0.035

Table 2 | Soil parameters. Measured soil parameters (n=3) in heath and fen bulk soils (± standard error of the mean). SOM=soil organic matter; DOC=dissolved organic carbon; TDN=Total dissolved nitrogen. SOM=soil organic matter; DOC=dissolved organic carbon; C_{mic}=microbial carbon; TDN=Total dissolved nitrogen.

	Heath		**Fen**	
	B horizon	**Permafrost**	**B horizon**	**Permafrost**
Gravimetric soil water content (%)	12.6 ± 2.5	25.1 ± 0.7	29.4 ± 3.3	51.3 ± 3.0
SOM (%)	4.8 ± 1.0	2.3 ± 0.6	8.5 ± 1.2	7.5 ± 1.3
pH	6.2 ± 0.1	7.3 ± 0.1	5.8 ± 0.2	5.9 ± 0.3
DOC (μg g^{-1} dw soil)	90.3 ± 14.6	104.3 ± 31.1	60.9 ± 10.4	71.2 ± 5.0
C_{mic} (μg g^{-1} dw soil)	69.0 ± 60.1	109.7 ± 6.2	144.8 ± 102.2	91.7 ± 85.3
NO_3-N (μg g^{-1} dw soil)	1.0 ± 0.3	0.7 ± 0.3	0.7 ± 0.2	0.09 ± 0.02
NH_4-N (μg g^{-1} dw soil)	1.0 ± 0.2	0.4 ± 0.04	0.8 ± 0.2	3.9 ± 1.3
TDN (μg g^{-1} dw soil)	14.8 ± 1.4	9.0 ± 1.3	17.0 ± 9.4	11.1 ± 0.9

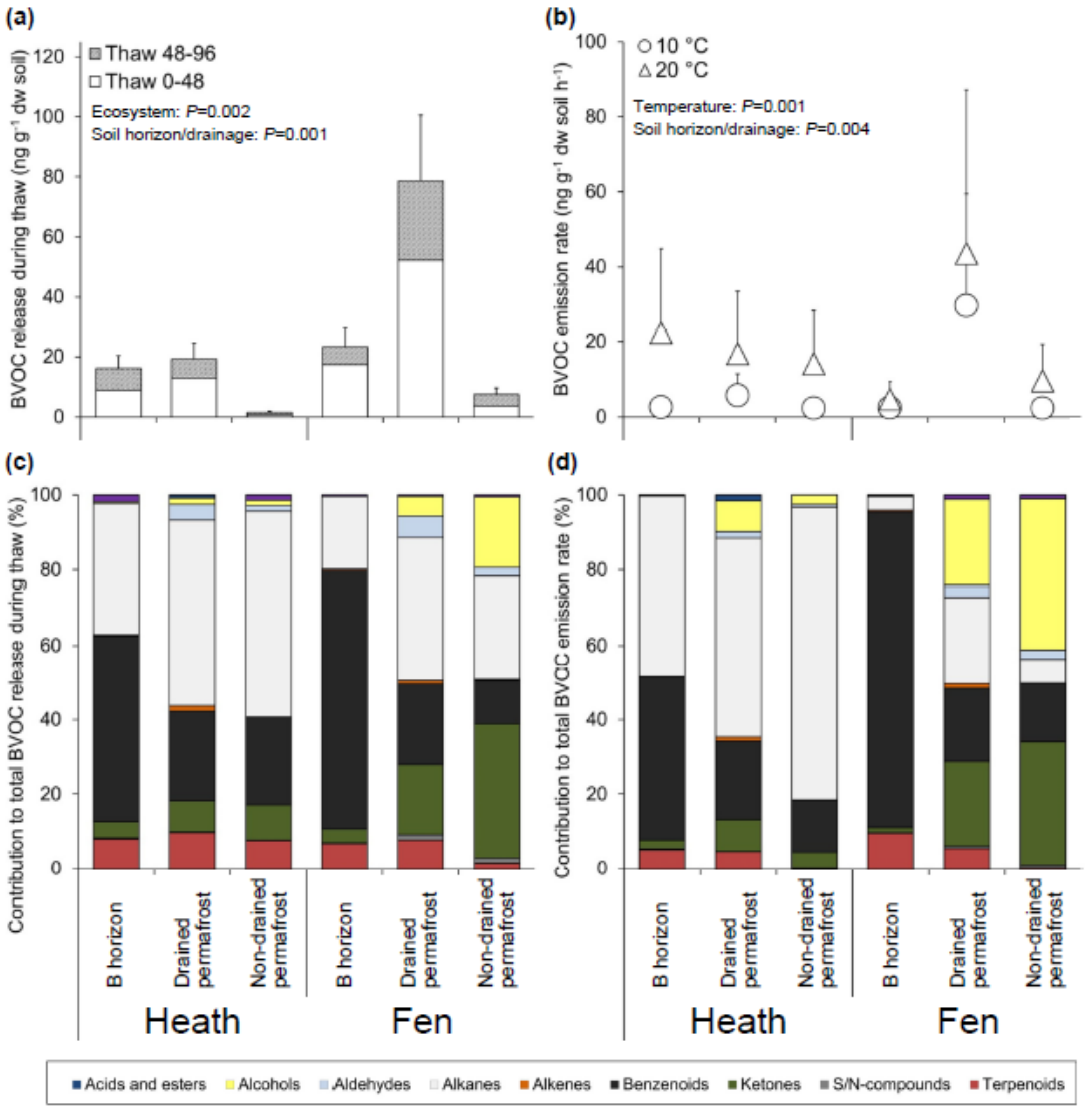
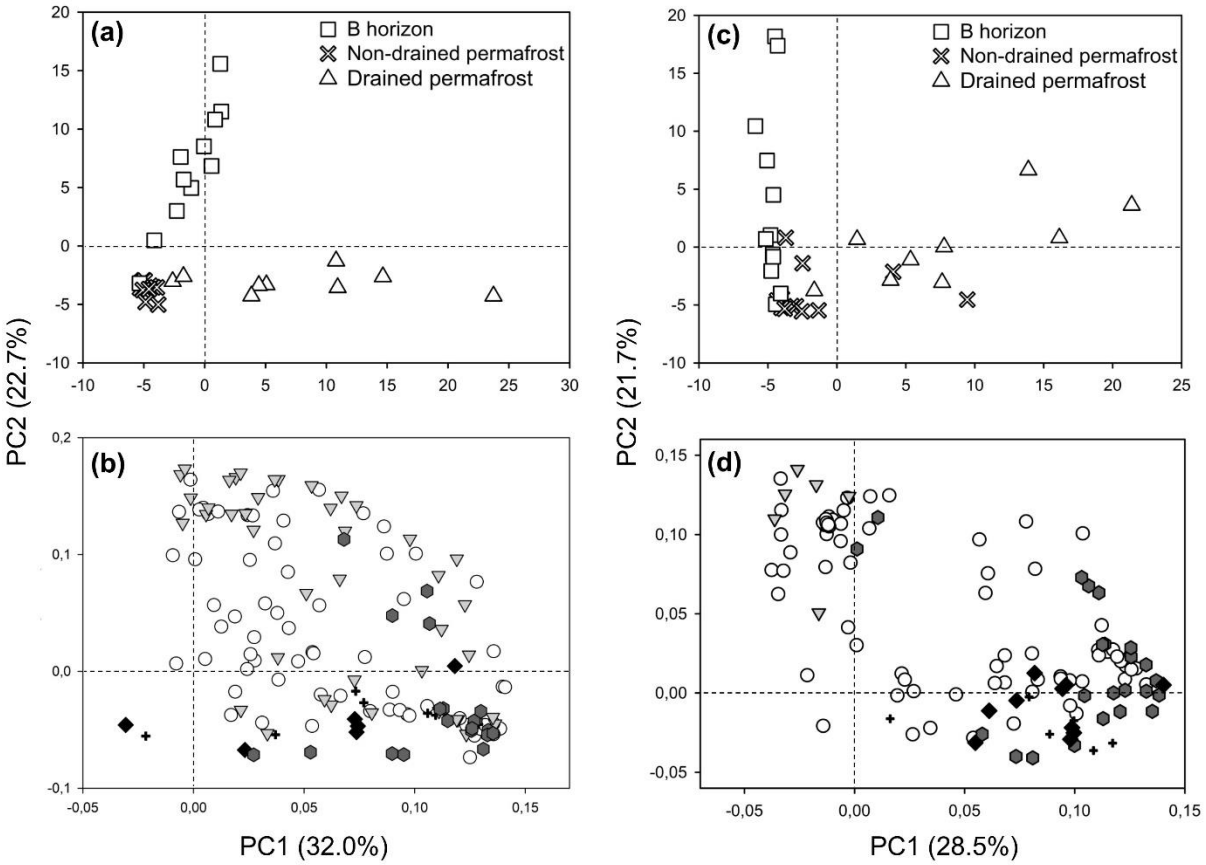
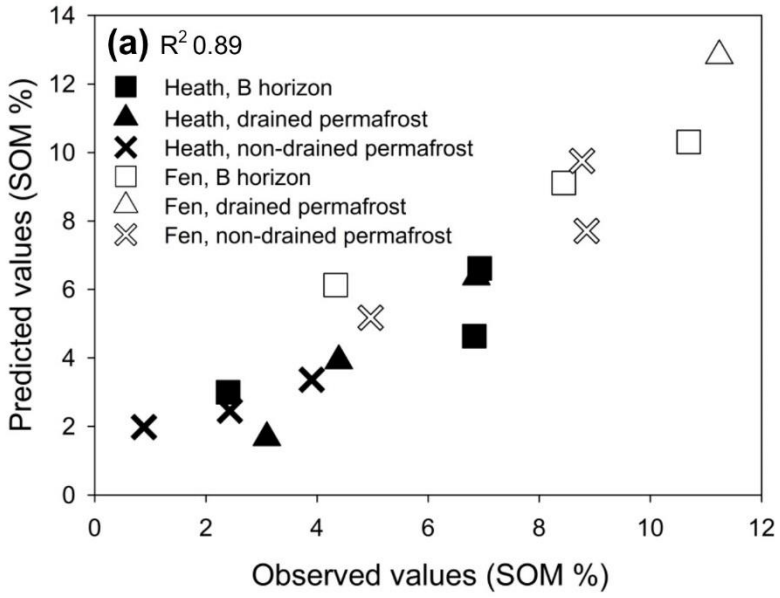


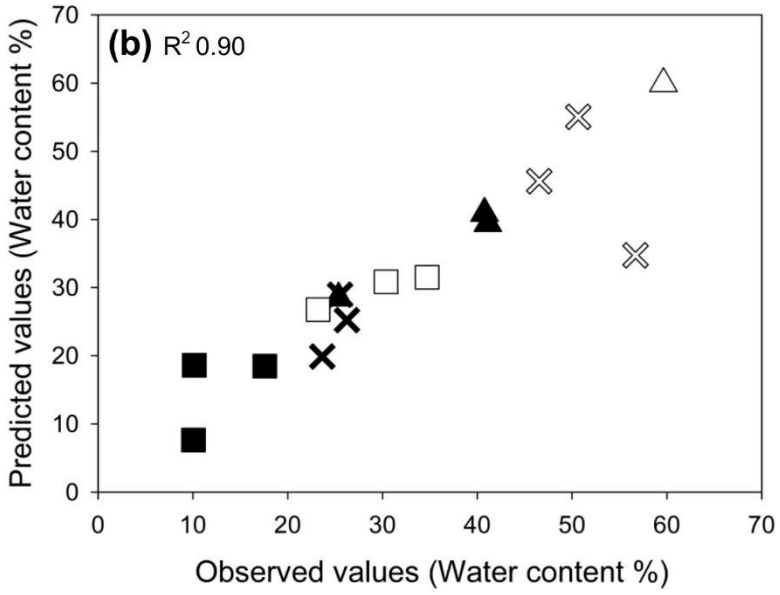
Figure 1 | Biogenic volatile organic compound (BVOC) release from thawed and warmed heath and fen soils. a) Accumulated release of total BVOCs during 0-48 h and 48-96 h from thawed soils. Error bars are the standard error of the mean (SE) of the total accumulation during 0-96 h. b) Relative contribution of the BVOCs accumulated during 0-96 h released from each group. c) Mean emission rate of total BVOCs at 10 °C and 20 °C (+ SE) from warmed soils. d) Relative contribution of total BVOCs to emission (average of emission rate at 10 °C and 20 °C). All measurements were performed in triplicates. Statistically significant *P*-values for the repeated measures analysis of variance (ANOVA) are shown in a and c. dw=dry weight.

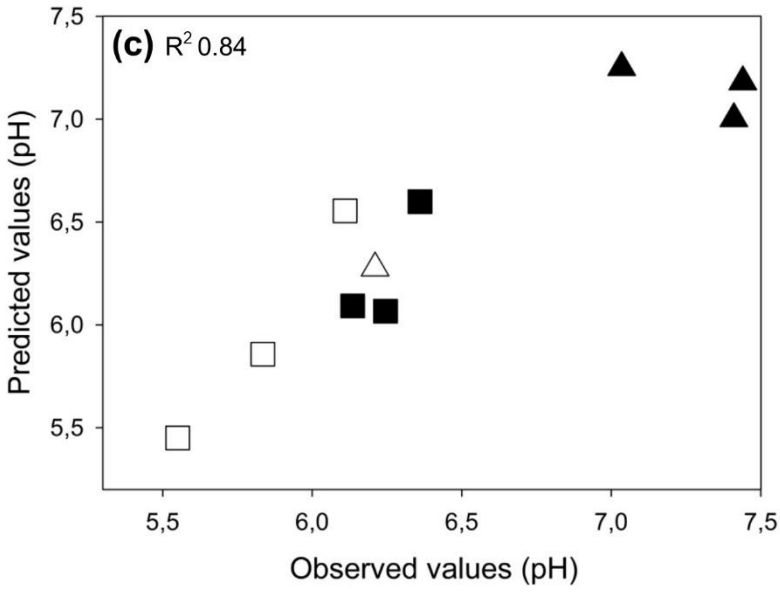


831

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 coordinal 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.


(a) R2 0.89
Heath, B horizon
Heath, drained permafrost
Heath, non-drained permafrost
Fen, B horizon
Fen, drained permafrost
Fen, non-drained permafrost
Predicted values (SOM %)
Observed values (SOM %)
0
2
4
6
8
10
12
14


(b) R2 0.90
Predicted values (Water content %)
Observed values (Water content %)
0
10
20
30
40
50
60
70


(c) R2 0.84
Predicted values (pH)
Observed values (pH)
5,5
6,0
6,5
7,0
7,5

839

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