



Soil uptake of VOCs exceeds production when VOCs are readily available

Yi Jiao^{a,b}, Magnus Kramshøj^b, Cleo L. Davie-Martin^{b,c}, Christian Nyrop Albers^d,
Riikka Rinnan^{a,b,*}

^a Center for Volatile Interactions (VOLT), Department of Biology, University of Copenhagen, Universitetsparken 15, Copenhagen Ø, 2100, Denmark

^b Terrestrial Ecology Section, Department of Biology, University of Copenhagen, Universitetsparken 13A, Copenhagen Ø, 2100, Denmark

^c Norwegian Institute for Air Research (NILU), The Fram Centre, NO-9296, Tromsø, Norway

^d Department of Geochemistry, Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, Copenhagen K, 1350, Denmark

ARTICLE INFO

Keywords:

Volatiles organic compounds
VOCs
Production
Uptake
Forest soil
Heath ecosystem

ABSTRACT

Volatile organic compounds (VOCs) are reactive gaseous compounds with significant impacts on air quality and the Earth's radiative balance. While natural ecosystems are known to be major sources of VOCs, primarily due to vegetation, soils, an important component of these ecosystems, have received relatively less attention as potential sources and sinks of VOCs. In this study, soil samples were collected from two temperate ecosystems: a beech forest and a heather heath, and then sieved, homogenized, and incubated under various controlled conditions such as different temperatures, oxic vs. anoxic conditions, and different ambient VOC levels. A dynamic flow-through system coupled to a proton transfer reaction-time of flight-mass spectrometry (PTR-ToF-MS) was used to measure production and/or uptake rates of selected VOCs, aiming to explore the processes and their controlling mechanisms. Our results showed that these soils were natural sources of a variety of VOCs, and the strength and profile of these emissions were influenced by soil properties (e.g. moisture, soil organic matter), oxic/anoxic conditions, and temperature. The soils also acted as sinks for most VOCs when VOC substrates at parts per billions levels (ranging between 0.18 and 68.65 ppb) were supplied to the headspace of the enclosed soils, and the size of the sink corresponded to the amount of VOCs available in the ambient air. Temperature-controlled incubations and glass bead simulations indicated that the uptake of VOCs by soils was likely driven by microbial metabolism, with a minor contribution from physical adsorption to soil particles. In conclusion, our study suggests that soil uptake of VOCs can mitigate the impact of other significant VOC sources in the near-surface environment and potentially regulate the net exchange of these trace gases in ecosystems.

1. Introduction

Natural ecosystems release about 1000 Tg of carbon as highly reactive volatile organic compounds (VOCs) to the atmosphere each year (Guenther et al., 2012). These VOCs can influence tropospheric air quality and the Earth's radiative balance through their contribution to the formation of hazardous ozone, aerosols, and cloud condensation nuclei (Carter, 1994; Petäjä et al., 2021). Plant foliage, which synthesizes and releases biogenic VOCs both constitutively and in response to stressors like heat, drought, or herbivore damage (Vickers et al., 2009; Li et al., 2019), is the main source of VOC emissions within ecosystems. Furthermore, plants also use VOCs for inter- and intra-species communication and signaling, such as attracting pollinators or deterring herbivores (Baldwin et al., 2006; Heil and Silva Bueno, 2007). As a result, aboveground VOC emissions have been extensively studied and

incorporated into many atmospheric chemistry models (Levis et al., 2003; Guenther et al., 2012; Makkonen et al., 2012). In contrast, soils, which form the underlying surfaces of ecosystems, have received relatively less attention, despite some studies suggesting they are potentially important bidirectional interfaces of VOC exchange (Asensio et al., 2007b, 2007c; Ramirez et al., 2010; Kramshøj et al., 2018; Trowbridge et al., 2020; Meischner et al., 2022; Mu et al., 2022).

The direction and magnitude of soil-atmosphere exchange of VOCs can vary among different sites and/or periods, dependent on the interplay of multiple concurrent source and sink processes (Asensio et al., 2007b; Faubert et al., 2012; Kramshøj et al., 2016; Trowbridge et al., 2020; Wester-Larsen et al., 2020). With regards to sources, the active root system of plants can synthesize and release significant amounts of VOCs (Lin et al., 2007; Rinnan et al., 2013; Delory et al., 2016). For example, a study on a subalpine forest floor estimated that root VOC

* Corresponding author. Center for Volatile Interactions (VOLT), University of Copenhagen, Universitetsparken 15, Copenhagen Ø, 2100, Denmark.
E-mail address: riikka@bio.ku.dk (R. Rinnan).

<https://doi.org/10.1016/j.soilbio.2023.109153>

Received 20 February 2023; Received in revised form 14 August 2023; Accepted 16 August 2023

Available online 17 August 2023

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emissions contributed an average of 53% of the total VOCs emitted from the soil (Gray et al., 2014). Alternatively, through microbial (Bäck et al., 2010; Gray et al., 2010; Lemfack et al., 2018) and abiotic processes (Huber et al., 2010; Jiao et al., 2022), soil organic carbon can also be converted to VOCs. The relative contribution of soil VOC production to ecosystem-scale VOC emissions varies across different ecosystems, seasons, and among different VOC species, from negligible (Hayward et al., 2001; Asensio et al., 2007b, 2007c; Greenberg et al., 2012) to considerable. For example, emissions of methanol, acetone, and acetaldehyde from the soil in a ponderosa pine forest account for 20–65% of their overall ecosystem fluxes (Schade and Goldstein, 2001). In an Amazon rainforest, soil sesquiterpene emission can contribute up to 50% of the production of ozone and other oxidation products (Bourtsoukidis et al., 2018).

VOC uptake is also considered to be an omnipresent process in soils (Rinnan and Albers, 2020). Multiple physical, chemical, and biological mechanisms can contribute to VOC uptake in soils (Tang et al., 2019). VOCs produced in soil or transported from the atmosphere can diffuse through soil pores where they may either be adsorbed onto soil particles or dissolve in soil water until an equilibrium is reached (Ruiz et al., 1998; Ahn et al., 2020). This physical sink is normally reversible, which means that the immobilized VOCs may be released back to the gaseous phase upon perturbations, such as temperature or moisture changes (Schade and Custer, 2004; Li et al., 2016). Abiotic processes can also contribute to the degradation of VOCs (Wilson and Jones, 1996; Chen et al., 2001; Konstantinou et al., 2001), although biotic processes can be expected to dominate in soil (Cleveland and Yavitt, 1998; Rinnan and Albers, 2020; Trowbridge et al., 2020). As carbon-containing molecules, VOCs serve as carbon and energy sources for some heterotrophic microbes, which thereby function as biological VOC sinks (Albers et al., 2018; Kramshøj et al., 2018; McGenity et al., 2018; Randazzo et al., 2020; Zhang et al., 2020). Biotic or abiotic processes that lead to degradation are usually irreversible and can therefore be considered as true VOC sinks in soil. In contrast to VOC production and emission from soil, these VOC uptake processes, that occur simultaneously in the soil, are even less explored (Rinnan and Albers, 2020).

Many factors, such as soil properties, ambient VOC concentrations, temperature, microbial community composition, ecosystem type, and their interactions, may collectively influence the source and sink processes (Asensio et al., 2007c; Tang et al., 2019; Meischner et al., 2022; Mu et al., 2022). For example, for some VOCs, including toluene, monoterpenes, and certain oxygenated VOCs, both abiotic and biotic uptake processes likely follow first-order kinetics in relation to their soil concentrations (Wilson and Jones, 1996; Schade et al., 2011). Microorganisms in the oxic layer of surface soils may also take up VOCs, such as methanol, ethanol, and acetone produced in the deeper anoxic layers, as they diffuse towards the atmosphere (Kramshøj et al., 2018). Soil moisture and temperature have been shown to impact various physical processes (such as adsorption, dissolution, and volatilization) as well as biological processes (including biodegradation by microorganisms and uptake by plants) related to VOCs in the soil (Asensio et al., 2007a; Kramshøj et al., 2019; Meischner et al., 2022). These factors ultimately determine the direction and strength of VOC fluxes. Previous observations on soil VOCs have only covered a small fraction of typical ecosystems and environmental conditions; more measurements from different biomes are therefore required to provide more robust bottom-up estimates and help to identify the factors that influence VOC fluxes, as well as the underlying mechanisms of the concurrent VOC source and sink processes in soils.

Here we assessed VOC production and uptake in soil samples collected from two contrasting temperate ecosystems: a beech forest and a heather heath. The samples were sieved, homogenized, and then incubated in a dynamic flow-through system and VOC exchange rates were measured using proton-transfer-reaction time-of-flight mass spectrometry (PTR-ToF-MS). We examined net VOC production rates as well as VOC uptake capacity upon amending the inlet gas with a gradient of

VOC concentrations. We also conducted incubations under oxic or anoxic conditions to assess the influence of soil oxygen status on VOC production and uptake, and under different temperatures to investigate how VOC production and uptake are influenced by increasing temperatures. We hypothesized that (1) soils from these ecosystems would emit a variety of VOCs and that the contrasting soils would have distinct emission profiles; (2) soils would take up VOCs when they are readily available and that the uptake would respond to VOC availability, i.e. uptake rate would be higher with elevated substrate availability; (3) oxic conditions would promote VOC uptake or suppress VOC emission; (4) increasing temperature would increase both the emission and uptake rate of VOCs.

2. Materials and methods

2.1. Soil sample collection

The soil samples were collected from two temperate ecosystems in Denmark: (1) a beech (*Fagus sylvatica* L.) forest located at Hareskoven (55°46'37.6"N, 12°23'42.9"E) characterized by a forest floor vegetation of *Mercurialis perennis* L., *Hepatica nobilis* L., *Convallaria majalis* L., and *Galium odoratum* (L.) Scop.; and (2) a heather (*Calluna vulgaris* (L.) Hull) heath at Tisvilde Hegn (56°01'17.9"N, 12°00'09.3"E) characterized by scattered *Empetrum nigrum* L., *Erica tetralix* L., and *Vaccinium uliginosum* L.

At each sampling site, the loose surface litter was removed prior to soil sampling. The surface layer of the soil (0–10 cm) was collected using brass corers (5 cm diameter) and then pooled and sealed in plastic bags (over 30 cores collected across ~5 m² at each site with a total mass of 4–5 kg per site). Stones, roots, and visible litter were removed from the cores, which were then stored in the dark at 5 °C for approximately 4 months before the experiments. Soils were homogenized and sieved through 5 mm mesh right before the experiment start to remove small stones, but to retain fungal hyphae and soil microstructure as intact as possible.

The soil samples were pooled, mixed, and homogenized to create a controlled experimental setup that allowed us to investigate the processes of VOC production and degradation under controlled conditions. This approach enabled us to focus on understanding the underlying processes and mechanisms, with no actual intention to quantify fluxes under natural conditions.

2.2. Analysis of soil properties

Gravimetric soil water content was determined by oven-drying soil at 70 °C until constant weight (approx. 24–48 h) and soil organic matter content was estimated by loss on ignition at 550 °C for 6 h. Total C and N concentrations were determined in the dried and ground soil with a EuroEA3000DF elemental analyzer (Eurovector, Pavia, Italy).

To extract dissolved C, N and P, 10 g soil samples were extracted in 50 ml deionized water in a rotary shaker for 1 h. The extract was then filtered through Whatman GF-D glass microfiber filters (Whatman Ltd., Maidstone, UK) and analyzed for pH. Dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) were measured with a TOC-L total organic carbon analyzer (Shimadzu, Kyoto, Japan). Nitrate (NO₃⁻) and phosphate (PO₄³⁻) concentrations were measured using an FIA STAR 5000 flow injection analyzer (FOSS Tecator, Höganäs, Sweden).

Microbial biomass C (Cmic), N (Nmic), and P (Pmic) were estimated by the fumigation-extraction method (Joergensen, 1996; Jonasson et al., 1996). To release microbial elements, soil samples were subjected to chloroform-fumigation for 24 h followed by extraction by water (Lipson and Monson, 1998) and analyses, as described above. Cmic, Nmic, and Pmic were calculated as the differences in DOC, TDN, and PO₄³⁻ between fumigated and non-fumigated extracts, respectively. A conversion factor (kEC) of 0.45 was used to compensate for incomplete extractability for C, whilst a kEC of 0.4 was used for N and P (Joergensen, 1996; Jonasson

et al., 1996).

2.3. Soil incubations

2.3.1. General experimental setup

Three days prior to the start of each experiment, 50-g soil samples were incubated at the target temperature in sealed glass jars (370 mL, pre-baked for cleanness) with lids fitted with valves for attachment of two Teflon lines (inlet and outlet). During the three days, the jars were constantly flushed with an inflow gas (300 mL min⁻¹) to maintain specific conditions: anoxic conditions were obtained using pure N₂ and oxic conditions using synthetic air containing 20% O₂ and 80% N₂. Both inflow gases were free of VOCs and CO₂. Different experiments were conducted to compare effects of temperature and different VOC availabilities while monitoring VOC fluxes using a dynamic flow-through setup.

In each experiment, eight sample jars and one empty blank jar were analyzed in series in a repeated automation batch over 3–6 h in total (Fig. S1, Table S1), with each jar being measured for 20–40 min. Clean inflow gas (either N₂ or synthetic air) was directed into the jar being measured by way of a gas flow controller in a liquid calibration unit (LCU-a, Ionicon Analytik, Innsbruck, Austria) at an inflow rate of 300 mL min⁻¹. Only one jar was measured at a time and the inflow air only passed through the jar being measured, while the other jars remained open but with no gas flow between measurements. The outflow air from the sample jars was directed into a PTR-ToF-MS (TOF-1000 *ultra*, Ionicon Analytik, Innsbruck, Austria) by way of PTFE solenoid valves (Cole-Parmer, Cambridgeshire, U.K.) used to direct the flow from a specific jar. Soil moisture was not controlled during the experiments.

A liquid mixture (water solution) containing 12 target VOCs (methanol, acetaldehyde, acetone, isoprene, 2-butanone, 2-methylfuran, toluene, furfural, *cis*-3-hexen-1-ol, benzyl alcohol, terpinolene, and linalool, see Table S2 for their concentrations) was introduced to the air stream by way of a liquid flow controller within the LCU-a, allowing us to control the concentrations of VOCs entering the sample jar headspace. Using this setup it was possible to detect VOC net emissions when no VOCs were added to the headspace and net uptake of VOCs by the soils when different VOC concentrations were introduced. The 12 target VOCs were carefully chosen by taking into account both their significance in the environment and practical considerations: these VOCs have been reported in soil studies earlier (Leff and Fierer, 2008; Zhao et al., 2016; Rossabi et al., 2018; Christodoulou et al., 2021; Meischner et al., 2022) and also possess adequate solubility in water.

We introduced VOCs at parts per billion (ppbv) levels at three concentrations, i.e., low, medium, and high (Table 1), to the inlet gas stream that was directed through the incubations in the following manner. For some introduced VOCs, such as methanol, isoprene, toluene, linalool, etc., their low to medium concentrations were comparable to the ambient atmospheric concentrations observed in some environments with significant sources (Arey et al., 1991; Harrison et al., 2001; Jacob et al., 2005; Jaars et al., 2014). Upstream from the incubation jars, the

inlet gas consisting of pure N₂ or model air entered the Liquid Calibration Unit (LCU, Ionicon, Austria), where liquid solutions containing VOCs of different concentrations were vaporized and added to the gas stream at a rate of 5 μL min⁻¹. The liquid VOC solutions were prepared by mixing a stock solution (Table S2) with double-distilled water (ddH₂O) in various proportions to obtain three different concentration levels: (1) low concentration, which consisted of 14.3% of stock solution and 85.7% of ddH₂O; (2) medium concentration, which consisted of 33.3% of stock solution and 66.7% of ddH₂O; and (3) high concentration, which was 100% stock solution. The soil VOC flux rates were measured based on the concentration differences of specific VOCs (e.g. methanol, acetaldehyde) between the soil incubations and the non-soil control. Positive fluxes represent emissions and negative fluxes represent uptake from the air. To minimize any potential carryover effects from previous VOC addition treatments, each jar was flushed with synthetic air at a flow rate of 300 mL min⁻¹ for 2.5 min between each measurement.

Automation of both the LCU-a gas and liquid flow rates, and switching of the PTFE solenoid valves was achieved via the PTR-ToF-MS software (IoniTOF 4.0, Ionicon Analytik, Innsbruck, Austria).

2.3.2. Differences between ecosystems and the effect of oxic vs. anoxic conditions

In the first experiment, differences between the ecosystems (forest and heath) and oxic/anoxic conditions in VOC fluxes were tested. The experiment was carried out at 13 °C, which was accomplished by incubating the jars containing soil samples in a climate chamber (Medilow M 260L, J.P. SELECTA s.a., Barcelona, Spain). There were four independent replicates (n = 4) for each ecosystem and condition (2 ecosystems × 2 conditions), i.e., soil samples were exchanged for each combination of ecosystem and oxic/anoxic condition.

2.3.3. Effect of temperature

In the second experiment, the effect of temperature (3 levels: 7 °C, 13 °C, or 19 °C, controlled through a climate chamber) on VOC fluxes was tested. The experiment was carried out only with the forest soil samples under oxic conditions, i.e. synthetic air flow-through. There were eight independent replicates (n = 8) for each temperature level, i.e., soil samples were exchanged at different temperature level.

2.3.4. Effect of VOC additions

The experiments described in 2.3.2 and 2.3.3 were first conducted without VOC addition to the inflow, so that the VOC emission rates were measured. Afterwards, these experiments were carried out under three VOC addition levels (low-medium-high), following the same setup as before, with which the potential uptake rates of VOC were measured.

2.3.5. Glass beads simulations

Potential adsorption of VOCs onto particle surfaces was explored using sterilized glass beads. Instead of soil, we used 50 g spherical glass beads (100% lead free soda lime, 1.5 mm diameter, Scientific Industries

Table 1

Concentrations of the 12 target VOCs in the inlet gas stream under low-, medium-, and high-addition settings.

Compound	Formula	Parent m/z	Low concentration [ppbv]	Medium concentration [ppbv]	High concentration [ppbv]
Acetone	C ₃ H ₆ O	58.04	1.24	2.89	6.68
<i>cis</i> -3-hexen-1-ol	C ₆ H ₁₂ O	100.16	1.33	3.10	9.30
Benzyl alcohol	C ₇ H ₈ O	108.14	3.08	7.18	21.55
Acetaldehyde	C ₂ H ₄ O	44.05	0.37	0.86	2.57
2-butanone	C ₄ H ₈ O	72.11	0.45	1.04	3.14
Isoprene	C ₅ H ₈	68.12	5.52	12.88	68.65
Toluene	C ₇ H ₈	92.14	0.60	1.40	4.20
Methanol	CH ₄ O	32.04	0.90	2.10	6.30
Linalool	C ₁₀ H ₁₈ O	154.25	1.65	3.84	11.52
Furfural (2-furaldehyde)	C ₅ H ₄ O ₂	96.08	0.50	1.16	3.48
2-methylfuran	C ₅ H ₆ O	82.10	0.35	0.82	2.46
Terpinolene	C ₁₀ H ₁₆	136.23	0.18	0.42	1.27

Inc., USA). The experiment was carried out under synthetic air flow-through at 13 °C with four independent replicates for each VOC addition level ($n = 4$).

2.4. VOC measurements by PTR-ToF-MS

Air from the jars was directed through a ¼" Teflon outlet tube to a high-resolution PTR-ToF-MS, where the VOC mixing ratios were monitored and recorded in real time. The PTR-ToF-MS required a sample flow of 100 ml min⁻¹, while the excess (~200 ml min⁻¹) passed through a vent line. The PTR-ToF-MS was operated at drift tube settings of 2.30 mbar, 500 V and 60 °C, with an E/N value at 108 Td, and a 5-sec resolution between the mass range of 30–257 a.m.u. A permeation tube containing 1,3-diiodobenzene added a constant signal in the mass spectrum at m/z 203.943 that was used to calibrate the mass scale.

Raw PTR-ToF-MS data were processed using the PTRwid software tool (Holzinger, 2015). PTRwid detected mass peaks in the measured spectra, applied a mass-scale calibration, and subsequently, calculated the mixing ratios of the identified masses.

Ion source contaminants (e.g., O₂⁺, NO₂⁺, HCO₂⁺, etc.) and known interferences (e.g., hydrate clusters, fragments of 1,3-diiodobenzene, etc.) were removed from the mass list. In total, 224 distinct protonated masses were detected in the measurements. Among them, the 12 target VOCs were identified and calibrated. For the other 212 masses, no external calibration was applied.

2.5. Calibration

The PTR-ToF-MS was calibrated regularly with a liquid standard (Ionicon, Innsbruck, Austria) containing a mixture of several VOCs at ppm level, vaporized and diluted in pure nitrogen using the LCU-a. The 12 target compounds in the gas standard were used to directly calibrate the mixing ratios of the PTRwid output. Before, during, and after the incubations, calibrations were performed as usual with the LCU-a connected directly to the PTR-ToF-MS.

2.6. Flux calculation

VOC fluxes were calculated based upon the equation below:

$$F_{\text{VOC}} = \frac{3600 (C_t - C_0) \cdot Q}{m} \quad (1)$$

Where, F_{VOC} is the flux rate of a specific compound, in the unit of nmol g dw (dry weight)⁻¹ hr⁻¹; Q is the flow rate through the sample jar, in the unit of mol s⁻¹; 3600 is the conversion factor from second to hour; m is the dry weight of the soil sample in the jar, in the unit of g dw; C_t is the stabilized VOC concentration in the sample jar, and C_0 is the VOC concentration in the blank jar, both in the unit of parts per billion by volume, ppbv. C_t and C_0 were calculated as the average value of the equilibrium PTR-ToF-MS reading (between 15 and 20 min after the flow) during each measurement.

We used the convention that positive fluxes represented VOC emissions from the soils, while negative fluxes represented VOC uptake from air to soil.

2.7. Statistical analysis

Differences in soil properties between the beech forest and heather heath soil samples were explored by ANOVA.

VOC emission and uptake data were processed separately. For emissions (positive fluxes with no VOC additions to the headspace during experiment), flux values were log-transformed in order to obtain homogeneous error-variances before conducting statistical analyses. For uptake (negative fluxes with VOC additions to the headspace during experiment), the absolute values of all uptake flux data were also log-

transformed. This allowed us to use the subsequent MANOVA and ANOVA models best suited for the experimental designs, instead of rank-based non-parametric tests.

First, to assess how VOC emission composition profiles may differ in different ecosystems (forest vs. heath) and under oxic/anoxic conditions, the log-transformed and unit variance-scaled VOC emission data of all the individual compounds (224 masses) were subjected to a principal component analysis (PCA) using SIMCA 16.0.1 (Umetrics, Umeå, Sweden). The effects of ecosystems and oxic/anoxic conditions on the PC scores were tested with analysis of variance (ANOVA).

To assess how the emission rates of the 12 target VOCs may differ in different ecosystems, and under oxic/anoxic conditions, we assessed their main effects and interactions using multivariate analysis of variance (MANOVA) with oxic/anoxic condition and ecosystems as fixed factors. If the MANOVA yielded a significant effect, we proceeded to assessing the effects on individual VOCs using ANOVA.

To test for the effects of ecosystems, oxic/anoxic conditions, and VOC addition levels (low, medium, high) on the uptake rates of the 12 target VOCs, we ran a MANOVA, which included main effects of the fixed factors ecosystems, oxic/anoxic condition, and VOC addition, as well as their interactions, and the calibrated uptake fluxes of the 12 VOCs as dependent variables. To account for the effect of repeated measurements across the different VOC addition levels, the soil ID number was included as a random factor in model. The model initially included all main effects as well as interactions between the different factors. The insignificant interactions were dropped stepwise starting from the highest-level interactions with a conservative threshold, $P > 0.2$, so that the interaction terms were removed only if they did not have any influence at all on the given variable. For significant factors in the MANOVA model, we proceeded to analyze the responses of each of the 12 VOCs separately using ANOVA. When the VOC addition level was significant, Tukey's HSD post hoc test was used to assess differences among the different VOC addition levels (low, medium, high).

For the temperature experiment, a full MANOVA model was constructed to assess the main effects and interactions between the fixed factors temperature (7 °C, 13 °C, 19 °C) and VOC addition (low, medium, high) on the calibrated uptake fluxes of the 12 VOCs as dependent variables. The model was optimized and ANOVA and Tukey's HSD post hoc test were applied as above.

Statistical analyses were conducted with IBM SPSS Statistics 24 and the significance level used was $\alpha = 0.05$.

3. Results

3.1. Soil properties

Soils from the two ecosystems, beech forest and the heather heath, showed significantly distinct physico-chemical properties (ANOVA, Table 2). The forest soil had significantly higher soil moisture and higher concentrations of carbon and nutrients (organic matter, NO₃⁻, PO₄⁻, DOC, TDN, total N and C) than the heath soil. Also microbial biomass carbon and nitrogen were higher in the forest soil, but the microbial phosphorus content was higher in the heath soil.

3.2. Soil VOC emissions

PCA on the emission rates of all individual masses revealed the relative emission profiles differed in the two different ecosystems and under oxic/anoxic conditions (Fig. 1a). The first PC, which explained 34.9% of the variance, differed significantly between ecosystems ($P < 0.05$, ANOVA); the second PC, which explained 19.2% of the variance, differed significantly between soil oxic and anoxic conditions ($P < 0.05$, ANOVA). There was no significant interaction between ecosystems and oxic/anoxic conditions, i.e. both ecosystems responded similarly to the oxic/anoxic conditions. Based on the loadings, most of the detected masses, including the 12 target VOCs, were relatively more

Table 2

Physicochemical properties of the soil samples collected from temperate beech forest and coastal heath heath. Notes: Values reported in the table are mean \pm S.E. (n = 6). SWC, gravimetric soil water content; SOM, soil organic matter; DOC, dissolved organic carbon; TDN, total dissolved nitrogen; Cmic, microbial biomass carbon; Nmic, microbial biomass nitrogen; Pmic, microbial biomass phosphorus. All variables were significantly different between the two ecosystems (ANOVA).

Ecosystem	SWC [%]	SOM [%]	NO ₃ ⁻ [$\mu\text{g g dw}^{-1}$]	PO ₄ ⁻ [$\mu\text{g g dw}^{-1}$]	DOC [$\mu\text{g g dw}^{-1}$]	TDN [$\mu\text{g g dw}^{-1}$]	Cmic [$\mu\text{g g dw}^{-1}$]	Nmic [$\mu\text{g g dw}^{-1}$]	Pmic [$\mu\text{g g dw}^{-1}$]	Total N [%]	Total C [%]
Beech forest	36.0 \pm 0.4	8.1 \pm 0.1	7.2 \pm 0.1	2.2 \pm 0.2	287.3 \pm 8.8	28.1 \pm 0.6	982.0 \pm 23.6	69.8 \pm 4.3	14.9 \pm 1.0	0.2 \pm 0.0	4.0 \pm 0.1
Heather heath	7.7 \pm 0.3	3.7 \pm 0.1	0.2 \pm 0.0	0.5 \pm 0.0	120.5 \pm 2.5	10.0 \pm 0.3	407.2 \pm 19.8	45.2 \pm 1.5	20.5 \pm 0.5	0.1 \pm 0.0	2.4 \pm 0.4

Table 3

The adsorption rates of VOCs onto glass beads observed under three different VOC addition levels. Values reported are means \pm the standard errors of the fluxes in the unit of nmol g dw⁻¹ hr⁻¹.

Compound	Low addition	Medium addition	High addition
Acetone	0.03 \pm 0.04	0.05 \pm 0.01	-0.01 \pm 0.02
cis-3-Hexen-1-ol	0.00 \pm 0.09	0.00 \pm 0.00	0.00 \pm 0.00
Benzyl alcohol	0.00 \pm 0.00	-0.31 \pm 0.00	-1.08 \pm 0.46
Acetaldehyde	-0.17 \pm 0.43	0.00 \pm 0.00	0.00 \pm 0.00
2-Butanone	-0.01 \pm 0.01	-0.01 \pm 0.00	-0.04 \pm 0.01
Isoprene	-0.04 \pm 0.04	-0.31 \pm 0.09	-1.29 \pm 0.54
Toluene	0.00 \pm 0.00	-0.03 \pm 0.00	-0.09 \pm 0.03
Methanol	-0.07 \pm 0.13	-0.05 \pm 0.15	-0.17 \pm 0.02
Linalool	0.01 \pm 0.03	-0.14 \pm 0.01	-0.48 \pm 0.17
Furfural	0.00 \pm 0.02	0.03 \pm 0.01	-0.06 \pm 0.04
2-methylfuran	0.00 \pm 0.00	0.00 \pm 0.00	-0.02 \pm 0.01
Terpinolene	0.00 \pm 0.00	-0.02 \pm 0.00	-0.08 \pm 0.03

characteristic to the emissions from the heath soils (Fig. 1b).

Both forest and heath soil showed net emissions of the 12 target VOCs in the absence of supplied VOCs in the inlet gas under the oxic conditions (Fig. 2). The MANOVA model on the emission rates of the 12 VOCs suggested that soil oxic/anoxic conditions had a significant effect on the overall emission rates ($P < 0.05$), the direction of which differed between VOCs. The emission rates of isoprene, methanol, furfural and 2-methylfuran were significantly, 70–135%, higher under anoxic than oxic conditions (averaged for forest and heath soils, ANOVA). In MANOVA, there was no interaction between the condition and ecosystem, and ecosystem had no overall effects. However, when

assessing differences for the individual VOCs with ANOVA, significantly higher emission rates for heath soil than forest soil (107–248%, averaged for both oxic and anoxic conditions) were observed for cis-3-hexen-1-ol, acetaldehyde, toluene, methanol, and furfural.

Among the 12 target VOCs, acetone had the highest emission rates at 2.6 ± 1.3 nmol g dw⁻¹ hr⁻¹ from the forest soils, and 8.0 ± 2.6 nmol g dw⁻¹ hr⁻¹ from the heath soils, followed by cis-3-hexen-1-ol, benzyl alcohol, acetaldehyde, and 2-butanone. Under anoxic conditions, acetone still showed the largest emission rates at 0.9 ± 0.1 nmol g dw⁻¹ hr⁻¹, and 1.9 ± 0.6 nmol g dw⁻¹ hr⁻¹ for the forest and heath soil, respectively, followed by cis-3-hexen-1-ol, benzyl alcohol and acetaldehyde.

In the experiment assessing the effects of temperature, for most compounds the emission rates showed increasing trends with temperature, but the statistical differences were often masked by high variance (Fig. 3). For linalool and terpinolene, the emission rate significantly increased from the lowest incubation temperature to the next and again from that to the highest temperature, with a 4–7 fold increase from lowest to highest temperature (Tukey's HSD test, $P < 0.05$). For cis-3-hexen-1-ol, toluene, and methanol, the emission rates were significantly increased by the highest temperature. For other VOCs, the trends were unclear. For the VOCs exhibiting a significant temperature response, their Q₁₀ values (emission rate change coefficient for each 10 °C warming) spanned the range of 1.28–5.51 (Table S3), with cis-3-hexen-1-ol, terpinolene, linalool, and methanol exhibiting the highest temperature sensitivities. For example, mean emission rates of cis-3-hexen-1-ol increased by 83% from 7 °C to 13 °C and by another 177% from 13 °C to 19 °C.

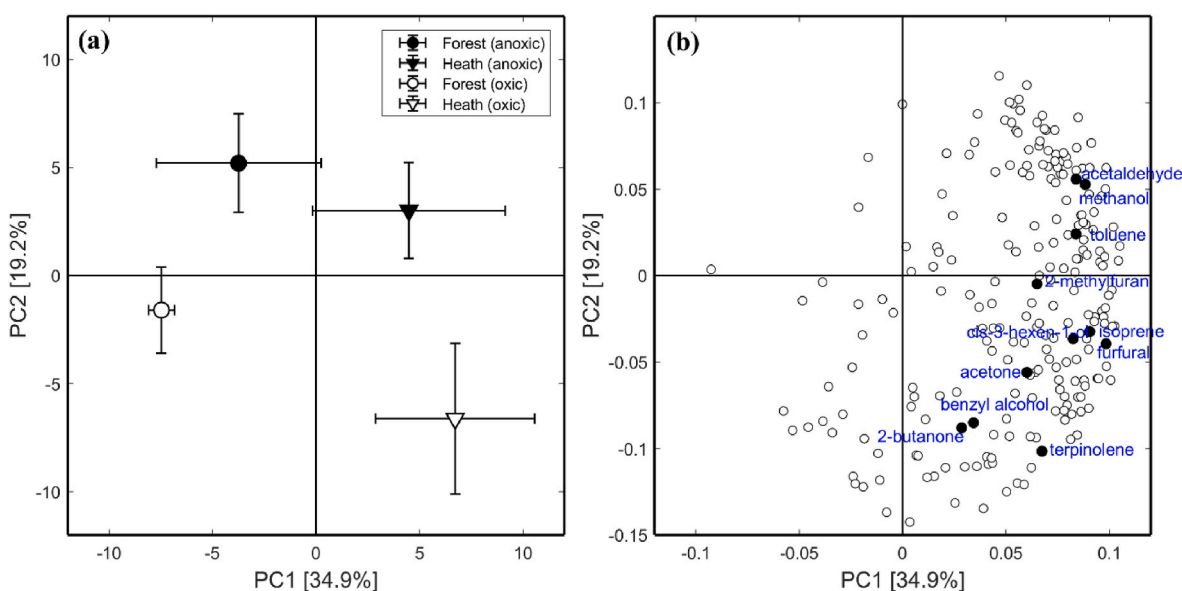


Fig. 1. Principle component analysis (PCA) of the emission profiles with 224 unique protonated masses. (a) PC1 and PC2 scores (mean \pm S.E., n = 4 for each ecosystem and soil oxic/anoxic condition), and (b) the corresponding loadings of all masses (open circles) with the 12 target VOCs (filled circles) annotated by their names. Variances explained by the PCs are provided in square brackets.

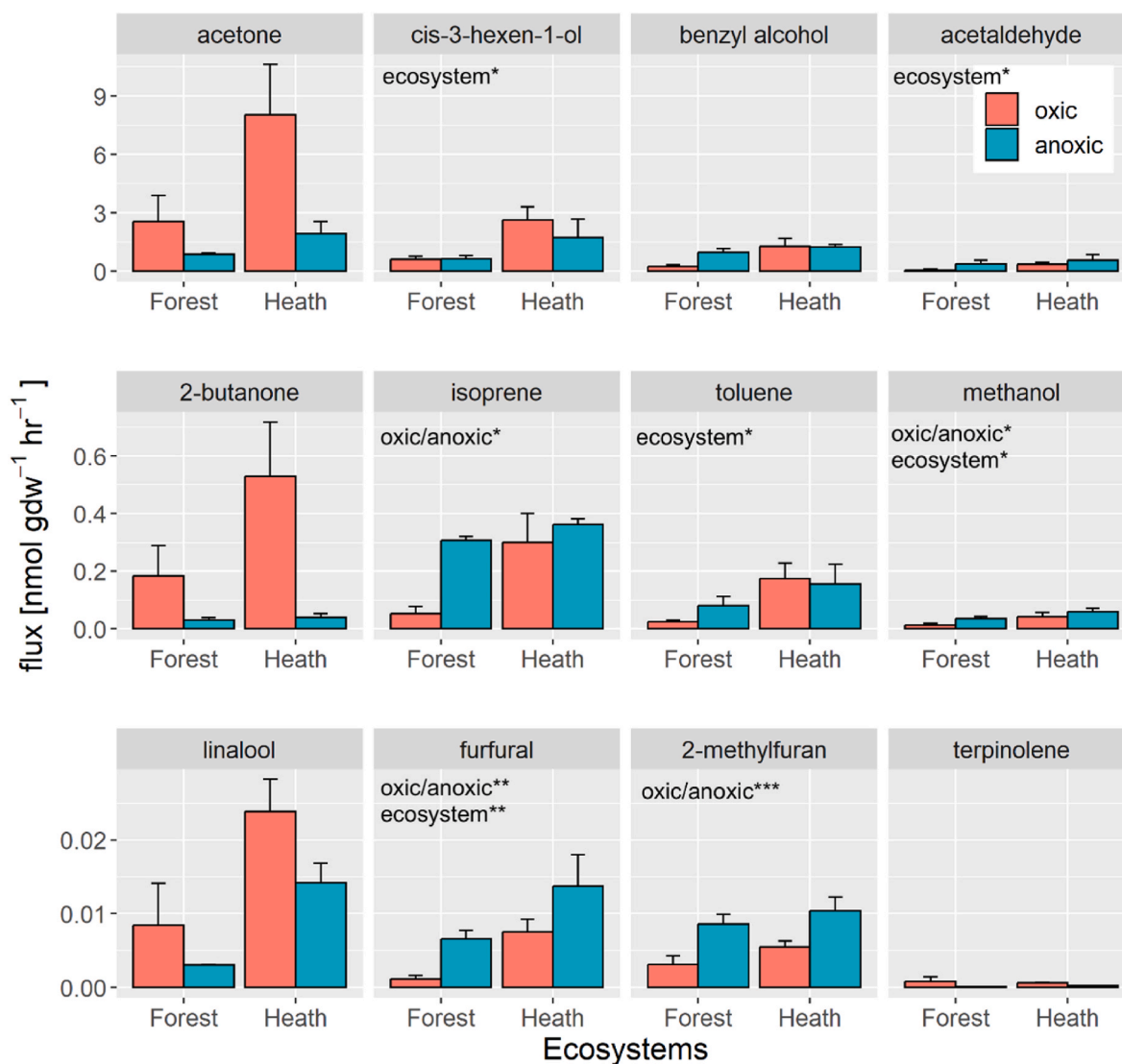


Fig. 2. Emission rates of 12 target VOCs from forest and heath soils under oxic and anoxic conditions. The bars represent the mean \pm S.E. ($n = 4$). Significant effect of ecosystems or oxic/anoxic conditions is shown at * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$.

3.3. VOC uptake in response to different levels of VOC availability

In the experiments where additional VOCs were supplied into the inlet gas stream, the MANOVA model showed that the ecosystem ($P < 0.05$), soil oxic/anoxic conditions ($P < 0.001$) and the VOC addition level ($P < 0.001$) had significant effects on the fluxes of the 12 target VOCs (Fig. 4). ANOVA analysis showed that the uptake of benzyl alcohol and toluene was lower in heath than forest soil (20% and 19% lower averaged across the addition levels, respectively), while the uptake rates of other compounds were not significantly different between the ecosystems. The uptake rates of *cis*-3-hexen-1-ol, linalool, and terpinolene were 24–33% higher under anoxic than oxic conditions. For toluene and acetaldehyde the difference was even larger, with 67% and 482% higher uptake rate under anoxic than oxic conditions. No ecosystems \times condition interactions were observed.

In general, the VOC uptake rates increased significantly with increasing amounts of VOCs supplied. In addition, there was a significant interaction between soil oxic/anoxic conditions and addition levels ($P < 0.001$), i.e., the responses to the VOC addition were different under oxic and anoxic conditions.

Under oxic conditions, when feeding the soils with additional VOCs, the soils showed net uptake of most VOCs. Only acetone, *cis*-3-hexen-1-

ol, acetaldehyde, and 2-butanone showed weak emissions under the low VOC addition level (Fig. 3). Under anoxic conditions, uptake of most VOCs was also observed for both ecosystems and most VOCs, except for acetone. For acetone, soil samples remained as sources (or fluctuated around zero) even with acetone additions, especially under low and medium addition levels, although the acetone emission rate consistently decreased as more acetone was supplied.

3.4. Temperature effect on VOC uptake

In the experiments where additional VOCs were supplied into the inlet gas stream, temperature and VOC addition levels both had a significant effect on overall VOC fluxes ($P < 0.001$, MANOVA) and the positive relationships between VOC uptake rates and temperature became more significant under higher VOC additions ($P < 0.001$ for the temperature \times addition interaction, MANOVA).

In general, uptake rates of most target VOCs increased as temperature went up (Fig. 5, Tukey's HSD test, $P < 0.05$). For example, under the high VOC addition level, significantly greater uptake rates of VOCs were observed at 19 °C for all VOCs, except for linalool and terpinolene with one outlying sample. Furfural (5.45), toluene (2.00) and *cis*-3-hexen-1-ol (1.89) uptake rates showed highest Q_{10} values (Table S3). For example,

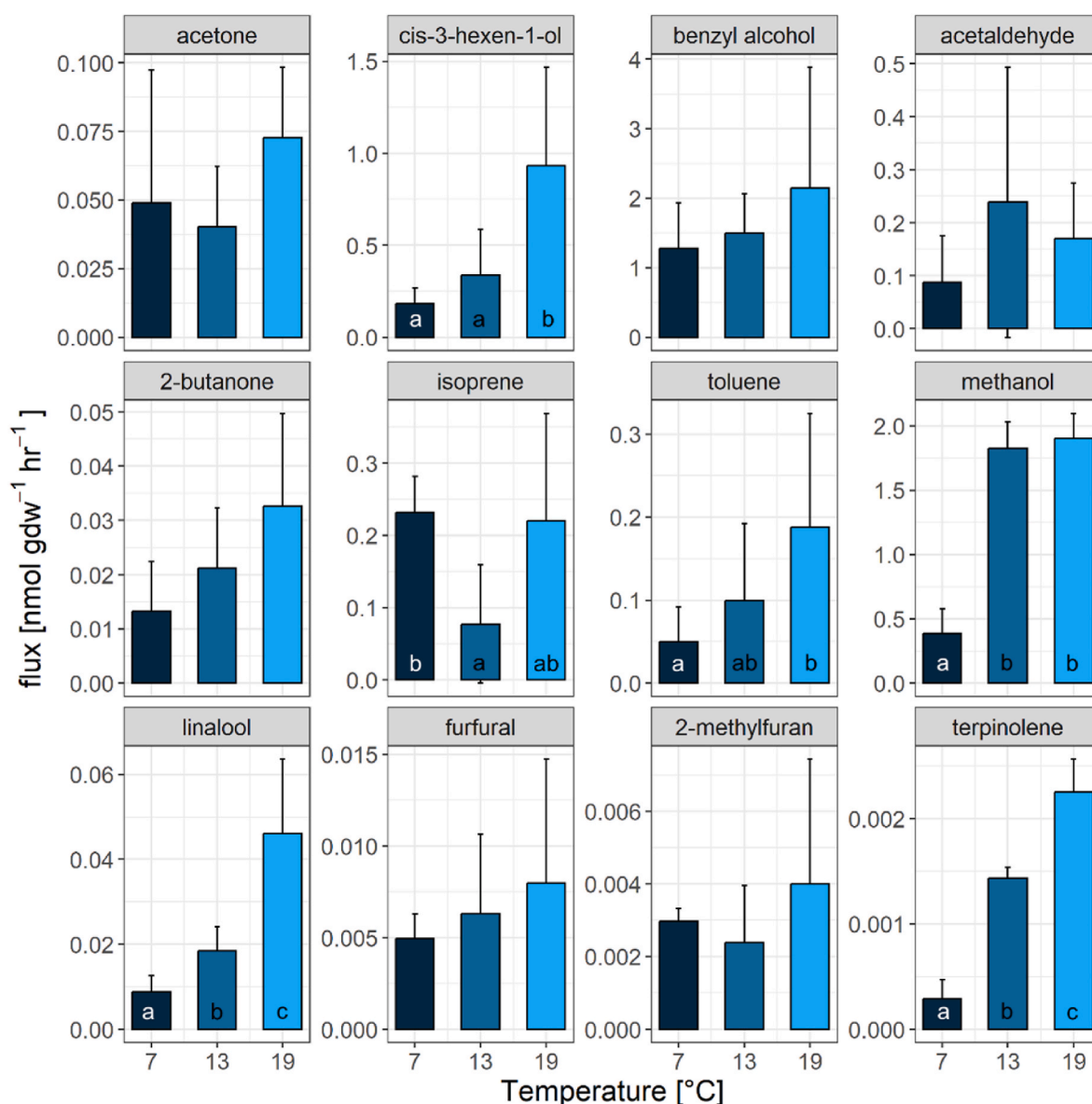


Fig. 3. Emission rates of the 12 target VOCs from the beech forest soils under different temperatures. The boxes show values for independent replicate samples ($n = 8$). Different lower-case letters indicate significant differences (Tukey's HSD test, $p < 0.05$). Note different y-axis scales.

mean emission rates of *cis*-3-hexen-1-ol increased by 83% from 7 °C to 13 °C and by another 177% from 13 °C to 19 °C.

3.5. Glass bead simulations

We observed that there was adsorption of VOCs to the glass beads, but this was on average less than 23% of the VOC uptake in soils (Table 3). In addition, in contrast to soil samples, the uptake rates did not respond to VOC addition levels (MANOVA, $P > 0.05$).

4. Discussion

4.1. VOC production in soils

We observed that soils from the beech forest and heather heath emitted a variety of VOCs. Compared to typical VOCs emitted by vegetation, lower molecular weight compounds, such as acetone, methanol, and acetaldehyde, were among the dominant VOCs, which has also been found in other soils, such as ponderosa pine and

agricultural fields (Schade and Goldstein, 2001; Schade and Custer, 2004; Abis et al., 2018; Bachy et al., 2018). A survey on VOC emissions from soils collected from an array of ecosystem types, including different forests, grassland, and cultivated land, noted that furfural and other furan compounds were often emitted in large amounts (Leff and Fierer, 2008). However, the study by Leff and Fierer (2008) used a gas chromatography-mass spectrometry analysis, which did not detect low-molecular weight compounds. We also observed furfural emissions in the present study, but the emission rates were much lower than those of other dominant compounds, such as acetone.

The two ecosystems showed contrasting emission profiles. The heath soil had higher net emission rates of *cis*-3-hexen-1-ol, methanol, acetaldehyde, and furfural than the forest soil. VOCs can be produced in soil through both microbial activity (Asensio et al., 2007c; Leff and Fierer, 2008; Gray et al., 2010) and abiotic geochemical processes (Huber et al., 2009, 2010), both of which use SOM as the substrate. Therefore, the contrasting VOC emission profiles may be attributed to the differences in soil properties of the two ecosystems. The soil water content in these two ecosystems differed significantly, potentially impacting microbial

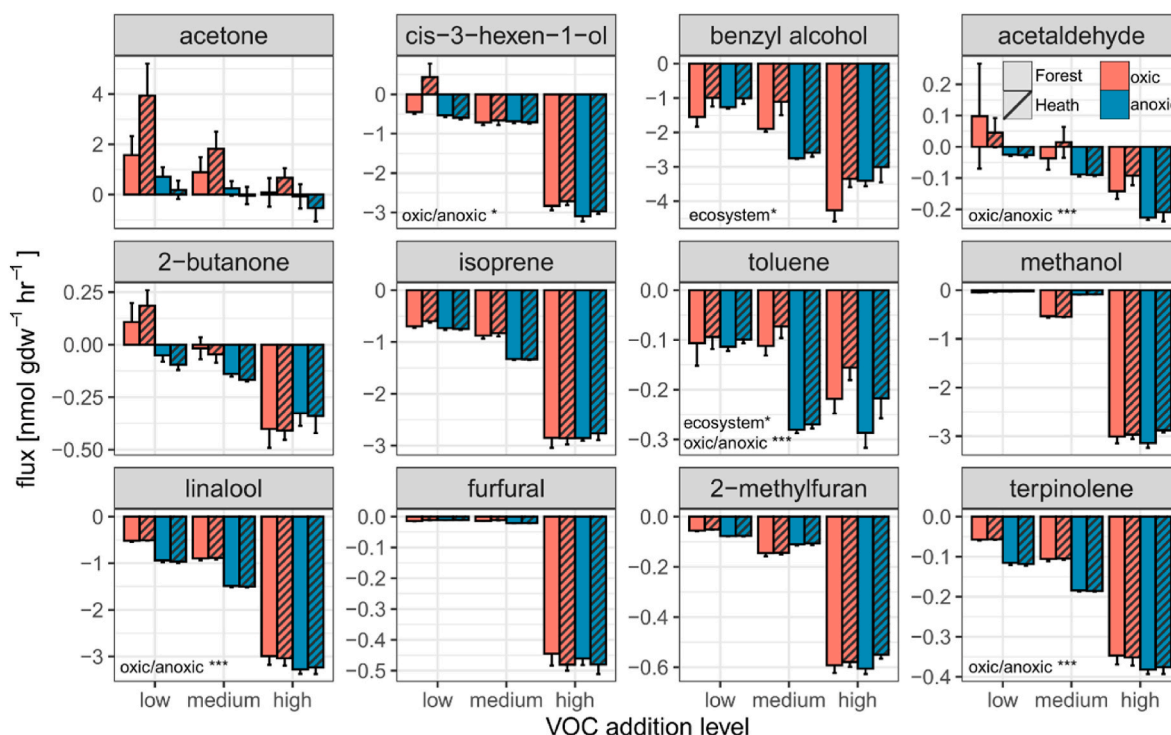


Fig. 4. Fluxes of 12 target VOCs in response to low, medium or high VOC additions under oxic or anoxic conditions. The bars represent the mean \pm S.E. ($n = 4$). Significant effects of ecosystems or oxic/anoxic conditions are shown at * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; ANOVA. VOC addition had significant effects on all compounds. Note different y-axis scales. Positive fluxes represent emissions and negative fluxes uptake.

activities and consequently VOC emission rates (Asensio et al., 2007a; Svendsen et al., 2016; Meischner et al., 2022). The forest soil was more nutrient rich and exhibited a higher soil moisture content, while the heath soil was poorer and drier. On the other hand, higher soil moisture would also promote microbial uptake of VOCs (Asensio et al., 2007a), which would result in lower net emission rates. The beech forest soil had lower VOC emission rates possibly because its higher soil moisture and nutrient contents maintained higher microbial activity, including the concurrent microbial VOC uptake, which lowered the net emission rates.

Our temperature experiment showed that soil temperature was an important influencing factor on soil VOC emissions, i.e., the higher the temperature, the more VOCs were emitted. If VOC production in soils exhibits exponential increase with temperature, soil emissions could become more significant under warming climate (Romero-Olivares et al., 2022). As both biological activity as well as abiotic process rates would increase with temperature, the observed temperature sensitivity does not reveal whether the production of VOCs was microbially mediated or abiotic. For some of the compounds that showed a clear temperature response, such as the terpenoids linalool and terpinolene, an abiotic formation mechanism seems highly unlikely, but release of adsorbed compounds upon the temperature increase cannot be excluded.

Different from some previous studies on soil VOCs associated with the presence of plant roots (Lin et al., 2007; Rinnan et al., 2013; Gray et al., 2014; Delory et al., 2016) or plant litter decomposition (Leff and Fierer, 2008; Ramirez et al., 2010; Abis et al., 2018), we used soil samples free of plant roots or litter for the VOC flux measurements, showing that VOCs could be produced directly from SOM. Together with other studies on soil VOC emissions (Asensio et al., 2007b, 2007c; Peñuelas et al., 2014; Bourtsoukidis et al., 2018; Rossabi et al., 2018), our results support the conventional view that soils may be widespread VOC sources in the ecosystem.

4.2. VOC uptake in soil

Different studies have also suggested that soils could be important VOC sinks (Asensio et al., 2007a, 2008; Ramirez et al., 2010; Chaignaud et al., 2018). In accordance with that, we showed that the soils took up VOCs when they were readily available. This uptake capacity responded to VOC availability, i.e., the uptake rates increased with elevated substrate availability. Therefore, soils within these ecosystems may act as VOC sinks if these compounds are significantly emitted from the aboveground vegetation and readily reach the soil through diffusion or turbulence, thereby regulating the net VOC fluxes of the ecosystems. Soils also degrade VOCs produced in soil or in the litter layer as earlier shown by Ramirez et al. (2010), VOCs emitted from the soil layer underneath, like thawing permafrost (Kramshøj et al., 2018), and if there is another significant VOC source, such as solid landfill waste (Randazzo et al., 2020).

Both biotic (Albers et al., 2018; Kramshøj et al., 2018) and abiotic pathways (Ruiz et al., 1998; Chen et al., 2001; Ahn et al., 2020) may be responsible for VOC uptake in soil. For example, VOCs can diffuse through soil pores and get adsorbed onto the surfaces of soil particles or dissolved into soil water (Ruiz et al., 1998; Ahn et al., 2020). Our glass bead tests suggested that other processes than this physical sink were predominantly responsible for the VOC uptake we observed. We also found a positive relationship between temperature and the VOC uptake rates, which further confirms that physical adsorption to soil particle or dissolution in soil water was unlikely the predominant sink, as the solubility of most of the VOCs decreases with temperature (Lin and Chou, 2006). On the other hand, it should be noted that the physical sink of natural soils may be greater than that observed in the glass bead simulations, which is attributed to the presence of water and the higher adsorption surface area of clay and organic materials present in soils. Moreover, these soil constituents often carry a negative charge, thereby enhancing the adhesive forces between soil particles and some VOC molecules (Serrano and Gallego, 2006).

Microbial utilization of the VOCs is likely the major responsible sink

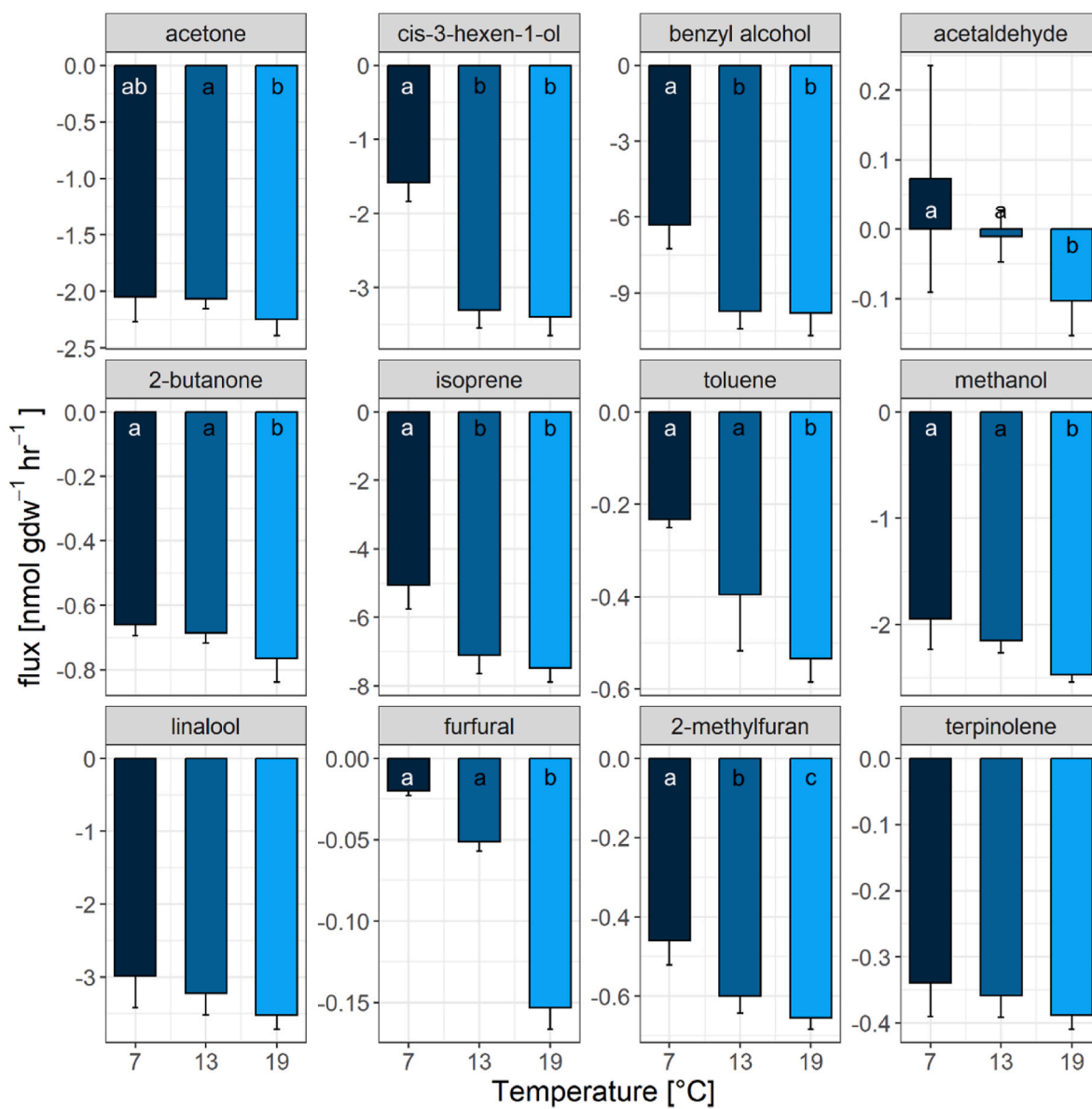


Fig. 5. Fluxes of the 12 target VOCs in the beech forest soils under different temperatures with high addition of VOCs. The boxes show values for independent replicate samples ($n = 8$). Different lower-case letters indicate significant differences (Tukey's HSD test, $p < 0.05$). Note different y-axis scales.

process in our study. Some heterotrophic microbes can utilize various VOCs as energy and/or carbon sources (Albers et al., 2018; Kramshøj et al., 2018; McGenity et al., 2018; Randazzo et al., 2020; Zhang et al., 2020). For example, it has been found that soils harbor ubiquitous methanol-oxidizing bacteria (Kolb, 2009; Stacheter et al., 2013). *Rhodococcus* sp. Strain AD45 and *Nocardia* have been shown to be capable of using isoprene as the sole source of carbon and energy, usually mediated by monooxygenase enzymes (Cleveland and Yavitt, 1997, 1998; van Hylckama Vlieg et al., 1998). The widespread *Pseudomonas putida* can mediate the degradation of benzyl alcohol through dehydrogenase (Shaw et al., 1993; Kasai et al., 2001). In a previous lab-based incubation of the soils collected from the same ecosystem we found microbe-mediated rapid mineralization of selected VOCs into CO_2 , including methanol and model compounds for terpenoids and aromatics (Albers et al., 2018). Thus, all of our 12 target VOCs likely have a microbial sink in the soil.

Abiotic mineralization processes could also slowly degrade or transform VOCs, e.g., through chemical reactions with NO_3^- and/or hydrogen peroxide (Chen et al., 2001; Atkinson and Arey, 2003; Insam

and Seewald, 2010), or through photolysis and other light-driven reactions (with OH radicals and O_3) in the surface of the soil. Nevertheless, the abiotic pathways of photolysis and light-driven reactions cannot explain the VOC uptake in our experiments, as incubations were conducted in dark climate chambers. The temperature relationships for VOC uptake observed in this study lend further support to the importance of microbial uptake.

Further examination of biotic vs. abiotic contributions could be accomplished through the comparison of responses in natural soils and effectively sterilized soils. However, sterilization of soils is challenging without directly impacting soil properties. Our attempts to sterilize soil samples using different methods, such as autoclaving and gamma-radiating (McNamara et al., 2003; Berns et al., 2008) have also not succeeded from a practical point of view: VOC emissions from sterilized soils have often far exceeded those from live soils. The enhanced emissions from sterilized soils may have been due to the release of microbial cell contents to the soil or VOC accumulation during thermal/radioactive degradation of SOM, leading to volatilization of compounds and a boost of emissions from turnover of the labile carbon by first

invader microbial species.

Among the 12 target VOCs that we amended to the headspace, acetone stood out as an exception. It consistently exhibited net emission, indicating that acetone production outweighed any potential sink effects. However, as the concentration of acetone in the inlet air increased, the net emission strength decreased, suggesting occurrence of acetone uptake. This finding aligns with a previous study by McBride et al. (2019), which also observed an increase in acetone metabolism through microbial respiration in response to higher acetone availability.

4.3. Effects of oxic/anoxic conditions

In the VOC emission experiment (no VOC additions into the inlet gas stream), contrasting VOC profiles and percent contributions were observed under oxic and anoxic conditions. Under anoxic conditions, higher emissions of methanol, isoprene, 2-methylfuran, and furfural were observed than under oxic conditions. The enhanced emissions under anoxic conditions may be a result of stimulated production, suppressed consumption, or a combination of both processes. Production of some VOCs (e.g., sesquiterpenes) is favored by anoxic conditions (Insam and Seewald, 2010; Bourtsoukidis et al., 2018). In contrast, degradation of VOCs is likely an aerobic process. Multiple aerobic prokaryotes have been identified to be able to oxidize and utilize methanol as energy and a carbon source (Kolb, 2009; Stacheter et al., 2013), which may result in lowered methanol emission rates under oxic conditions. Oxic conditions can also facilitate the degradation of some aromatic hydrocarbons (e.g., toluene) (Scheutz et al., 2004).

In the VOC uptake experiment (with VOC additions into the gas stream), the uptake rates of toluene, terpinolene and linalool were higher under anoxic than oxic conditions, suggesting that microbes utilizing these specific VOCs would favor anoxic over oxic conditions. However, as discussed above, VOCs degradation likely requires oxic conditions (Kolb, 2009; Stacheter et al., 2013). In our study, the anoxic conditions were introduced only three days prior to the start of the experiment, which may not have been a long enough duration for soil anaerobes to become active as well as for soil aerobes to completely terminate their metabolism (Pedraz et al., 2020). Consequently, what we observed could be a mixture of VOCs exchanged in/out by aerobic and anaerobic microbial communities under the increasing and persistent stress of low oxygen levels. Even in well-aerated upland soils like those in our study, short-term anoxic microsites could occur naturally from time to time (Keiluweit et al., 2018; Lacroix et al., 2022). Our study therefore suggests that the direction and magnitude of soil VOC fluxes may fluctuate as the anoxic microsites develop.

In summary, in this study, we collected and homogenized the soil samples from two typical temperate ecosystems to create a controlled experimental setup that allowed us to investigate the processes of VOC production and degradation under controlled conditions. Our study highlights the potential role of soil as an important bidirectional interface exchanging VOCs in the ecosystem. The direction and magnitude of the VOC fluxes vary under different environments and VOC availabilities, and soil may potentially regulate the net VOC fluxes of the ecosystem.

Declaration of competing interest

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

Data availability

Data archived on Zenodo with a doi number (10.5281/zenodo.8026818) with permanent public free access.

Acknowledgment

This study was jointly supported by European Research Council under European Union's Horizon 2020 research and innovation programme (grant No. 771012 to R.R.), Elite Research Prize of the Danish Ministry for Higher Education and Science (grant No. 9095-00004 to R. R.), and Danish National Research Foundation (Center for Volatile Interactions, grant No. DNR168 to R.R.). Y.J. was supported by Marie Skłodowska-Curie Action Postdoctoral Fellowship under EU's Horizon Europe research and innovation programme (agreement No. 101061660). The authors express their gratitude to the three anonymous reviewers for their constructive comments and valuable feedback, which significantly enhanced the quality of the manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.soilbio.2023.109153>.

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