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**Boreal wetland and  
forest floor VOC  
emissions**

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# $C_2$ - $C_{10}$ hydrocarbon emissions from a boreal wetland and forest floor

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## Abstract

Emissions of various C<sub>2</sub>-C<sub>10</sub> hydrocarbons and halogenated hydrocarbons from a boreal wetland and Scots pine forest floor were measured by static chamber technique in south-western Finland. Isoprene was the main non-methane hydrocarbon emitted by the wetland but also small emissions of ethene, propane, propene, 1-butene, 2-methylpropene, butane, pentane and hexane were detected. The isoprene emission from the wetland was observed to follow the commonly used isoprene emission algorithm. The mean emission potential of isoprene was 224 μg m<sup>-2</sup> h<sup>-1</sup> for the whole season. This is lower than the emission potentials published earlier and probably least partly due to the cold and cloudy weather during the measurements. No emissions of monoterpenes or halogenated hydrocarbons from the wetland were detected. Highest hydrocarbon emissions from the Scots pine forest floor were measured in spring and autumn. Main emitted compounds were monoterpenes. Isoprene emissions were negligible. Highest monoterpene emissions were measured in spring after the snow had melted. Emissions dropped in the summer and increased again in autumn. The total monoterpene emission rates varied from zero to 373 μg m<sup>-2</sup> h<sup>-1</sup>. Probable source for these emissions is decaying plant litter. Also small emissions of chloroform (100–800 ng m<sup>-2</sup> h<sup>-1</sup>), ethene, propane, propene, 2-methylpropene, cis-2-butene, pentane, hexane and heptane were detected.

## 1. Introduction

The boreal zone covers large areas in the northern hemisphere and is the largest forested region on Earth. In addition to forests, wetlands are a typical feature of the boreal zone. Meanwhile the non-methane hydrocarbon (NMHC) emissions from the boreal forest ecosystems have been studied quite intensively (e.g. Janson, 1993, Hakola et al., 1998, 2001, 2003, 2005; Rinne et al., 2000; Janson and De Serves, 2001; Tarvainen et al., 2005), the data on the wetlands is scarce. Janson et al. (1999), Jansson

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and De Serves (1998) and Haapanala et al. (2005) have shown that boreal wetlands are a significant isoprene source. In a study by Rinnan et al. (2004) various VOCs, emitted from wetland microcosm samples taken from a wetland in Finland, were identified.

5 The studies on the VOC emissions from forest ecosystems have mostly been concentrated on the emissions from tree canopies, as the emissions from e.g. decaying leaf and needle litter has been assumed small compared to the canopy emissions. This has been demonstrated also in the studies by Janson (1993), Janson et al. (1999), and Hayward et al. (2001), who found monoterpene emissions from the forest floor to be  
10 insignificant compared to the emissions from trees in summer. However, during the other seasons forest floor may have an important role. Isidorov et al. (2003 and 2005) have found that decomposing leaf litter emits several different VOCs. These emissions would occur during autumn and again in spring after melting of snow and the ground.

15 Wetlands and forest floor may also be a significant source for the halogenated hydrocarbons which have been observed to be emitted e.g. by wetlands and forest floor in Ireland (Dimmer et al., 2001), by coastal salt marshes in California (Rhew et al., 2000) and by forest floors in Denmark and Netherlands (Haselmann et al., 2000; Hoekstra et al., 2001). Soil emissions have been estimated to be major contributor to the atmospheric chloroform burden (Laternus et al., 2002). However, due to the lack of emission  
20 data estimates are still highly uncertain.

In this study emissions of different C<sub>2</sub>-C<sub>10</sub> hydrocarbons and halogenated hydrocarbons from a boreal wetland and forest floor were identified and their fluxes to the atmosphere were quantified.

## 2. Materials and methods

25 Forest floor measurements were conducted at Hyytiälä SMEAR II measurement station (61°51' N, 24°17' E, 180 m a.s.l.) in the south boreal zone in southern Finland and the wetland measurements were carried out at Siikaneva fen located a few kilometers

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west from the SMEAR II station. The forest at the forest floor measurement site is dominated by Scots pine (*Pinus sylvestris* L.) with some deciduous trees, such as European aspen (*Populus tremula*) and birches (*Betula pendula* and *B. pubescens*). The ground vegetation consists mainly of shrubs (*Vaccinium myrtillus*, *V. vitis-idaea*, *Oxalis acetosella*). The forest floor at the site is covered with mosses (*Dicranum polysetum*, *Pleurozium schereberi*, *Hylocomium splendens*). Soil type is Haplic Podzol. Siikaneva is an open fen and vegetation is dominated by mosses (*Sphagnum balticum*, *S. majus* and *S. papillosum*), sedges (*Carex rostrata*, *C. limosa*, *Eriophorum vaginatum*) and Rannoch-rush (*Scheuchzeria palustris*). The fen is surrounded by coniferous forests. The measurements at Siikaneva were performed between June and October 2004 and at Hyytiälä between April and October in 2004 and between April and June in 2005. Because of the lack of warm and sunny days in 2004 data, one additional measurement was conducted at Siikaneva on 18 August 2005.

Measurements were conducted using static chamber technique on five different stainless steel collars (60 cm×60 cm) in Siikaneva and on two different collars in Hyytiälä. The collars were installed to the ground half year prior to the measurements and remained undisturbed throughout the measurement periods. Two different chambers were used; one with dimensions of 60 cm×60 cm×50 cm and another with 60 cm×60 cm×25 cm. Both chambers were covered inside with transparent Teflon film and a Teflon-membrane pump was used to recycle the air in the chamber.

VOC emission was determined from the increase of the concentration in the chamber during the closure. Three samples were taken and analyzed during each closure. The concentration increase was normalized to the plot area and time. Time intervals between the three samples were varied from 5 min to 50 min in order to find the optimum sampling time. In most of the cases 10 min was found to be the best compromise. An example of the increase in concentration in the chamber can be seen in Fig. 1. If the linearity of the concentration increase was poor (correlation coefficient ( $R^2$ ) between concentrations and time less than 0.8), results were not used in flux calculations. Because of too long sampling interval of some of the samples in the beginning of the

measurement period in 2004, emissions had to be calculated by using only first two samples in these cases.

Some of the VOCs, such as monoterpenes, are very reactive towards ozone, which can pose problems in the emission measurements. However, in the studies of Janson et al. (1999) ozone has been found to disappear by dry deposition within 1 min after the closure of a Teflon chamber. Therefore even though any ozone removal techniques were not used in this study, ozone should not be a problem. In 2005 comparisons with a dynamic chamber system, where ozone was removed with MnO<sub>2</sub> coated copper nets, were conducted. VOC emissions measured by these two systems were at same level and this gave more confirmation that ozone was not a problem in static chamber measurements.

Air temperature in the chambers was observed to increase during the closure. In the studies in Ireland Dimmer et al. (2001) measured increases of air temperature in the chambers from 5°C to 15°C, but the maximum increase in soil temperature at 10 cm depth was only 0.2°C. In our study the increase of air temperature was found to be significant (>2°C) only on sunny and warm days. As the summer 2004 was exceptional cold and rainy this was not a serious problem in most of the measurements in this study.

VOC samples from the chambers were taken using Tenax TA-Carbopack B adsorbent tubes and 0.85 L stainless steel canisters. From the adsorbent tubes C<sub>5</sub>-C<sub>10</sub> hydrocarbons (alkanes, alkenes, aromatic HC's, and terpenes) and some halogenated hydrocarbons (1,2-dichloroethane, chloroform, 1,1,1-trichloroethane, tetrachloroethane, trichloroethene, tetrachloroethene) were analysed using a Perkin Elmer ATD-400 thermal desorption unit together with a gas chromatograph (HP-5890) with an HP-1 column (60 m, i.d. 0.25 mm) and a mass spectrometer (HP-5972). In 2004 samples were analysed in SCAN mode but in 2005 more sensitive SIM (selective ion monitoring) mode was used. Therefore detection limits in 2005 were lower than in 2004. Lighter C<sub>2</sub>-C<sub>6</sub> and halogenated hydrocarbons were analysed from canisters using a gas chromatograph (HP-6890) with Al<sub>2</sub>O<sub>3</sub>/KCl PLOT column. After the column, sample flow was split into two different detectors; C<sub>2</sub>-C<sub>7</sub> hydrocarbons were detected using

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5 a flame ionization detector (FID) and halogenated hydrocarbons (chloromethane, CFC-12, CFC-11 and CFC-113) with an electron capture detector (ECD). Before the analysis water and CO<sub>2</sub> were removed using a K<sub>2</sub>CO<sub>3</sub>/NaOH-drier. Subsequently the sample (ca. 500 ml) was concentrated using two liquid nitrogen traps. For adsorbent samples  
10 five-point calibration was performed using liquid standards in methanol solution. For canister samples gas-phase standards from NPL (National Physical Laboratory, UK) for hydrocarbons and from NOAA (National Oceanic and Atmospheric Administration, USA) for halogenated hydrocarbons were used. A blank test was conducted by covering a frame with Teflon film. No production or degradation of measured compounds was detected.

### 3. Results

#### 3.1. Wetland emissions

15 Main non-methane hydrocarbon emitted by the wetland was isoprene. However, also small emissions of ethene, propane, propene, butane 1-butene, 2-methylpropene, pentane and hexane were detected (Table 1). Summer 2004 was very rainy and cold in Siikaneva and the measured emission rates were relatively low, the highest measured emission rate being 53  $\mu\text{g m}^{-2} \text{h}^{-1}$ . In 2005, when measurements were conducted only on one warm and sunny day, emission rates varied between 50 and 103  $\mu\text{g m}^{-2} \text{h}^{-1}$ .

20 Isoprene emissions from the vegetation are light and temperature dependent. This dependence can be described by algorithms presented by Guenther et al. (1993) and Guenther (1997). Standard emission potential, obtained by linear fitting of emission rates to the light and temperature activity factors ( $C_T \cdot C_L$ ) of the isoprene emission algorithm, was 224  $\mu\text{g m}^{-2} \text{h}^{-1}$  (Fig. 2). Coefficient of correlation between measured emission rates and light and temperature activity factor ( $C_T \cdot C_L$ ) of Guenther algorithm  
25 was 0.69 (Fig. 2). While temperature and PAR can explain much of the variation also other factors can have an effect. For example, seasonal development and water con-

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5 tent may explain part of the variation (Janson and De Serves, 1998). Standard ( $T=30^{\circ}\text{C}$  and  $\text{PAR}=1000\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$ ) emission potentials of isoprene were calculated for each measurement separately using the isoprene emission algorithm. Daily average values are shown in Fig. 3. The results indicate that highest standard emission potentials are measured in August. However, more measurements are needed to verify this conclusion.

10 In a VOC flux study by the REA technique on Siikaneva in 2004 and 2005, the average standard emission potential of isoprene was found to be  $680\ \mu\text{g m}^{-2}\ \text{h}^{-1}$  (Haa-panala et al., 2005) which is several time higher than found in this study. However, Haa-panala et al. (2005) observed that for low  $C_T\text{-}C_L$  values ( $<0.2$ ), the emission potential was lower, only  $330\ \mu\text{g m}^{-2}\ \text{h}^{-1}$ . This value is closer to the emission potential obtained this study, in which the  $C_T\text{-}C_L$  values were low. Other possible reason for differences in the measured emissions is that the REA technique measures flux from much larger area than the chamber technique. However, using the chamber technique Janson and De Serves (1998) found also higher emission potentials ( $700\pm 400\ \mu\text{g m}^{-2}\ \text{h}^{-1}$ ) from the *Sphagnum* fens in Sweden and Finland in June–August 1997, but their measurements were also conducted in warm and sunny conditions.

20 No clear emissions of monoterpenes, aromatic hydrocarbons or other larger volatile organic compounds ( $>C_5$ ) were detected although Rinnan et al. (2004) found emission of 45 different  $C_4\text{-}C_{10}$  volatile organic compounds including aromatic hydrocarbons and monoterpenes from microcosms taken from a Finnish wetland. However, they did not quantify the emissions and raised a question concerning possible contamination of the microcosms during transportation.

25 Despite of a special effort, no emissions of halogenated hydrocarbons were detected. In the studies of Dimmer et al. (2001) significant emissions of  $\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{CH}_3\text{I}$  and  $\text{CHCl}_3$  were found to be emitted from wetlands and forest floor in Ireland and Varner et al. (1999) have reported emissions of  $\text{CH}_3\text{Cl}$  and  $\text{CH}_3\text{Br}$  from two wetlands in Northeastern United States, both dominated by *Sphagnum* and *Carex* species.

To study the origin of the VOC emissions all sedges were removed from one of

the plots. This did not change the magnitude of the emissions. Standard emission potential of isoprene from the plot containing only mosses was  $127 \mu\text{g m}^{-2} \text{h}^{-1}$ , which is at the same level as the average value of all the plots  $224 \mu\text{g m}^{-2} \text{h}^{-1}$ . From the plot where both green mosses and sedges were removed, almost no emissions were detected (emission potential  $<1 \mu\text{g m}^{-2} \text{h}^{-1}$ ). This indicates that the *Sphagnum* moss is the main source of the isoprene emitted by the fen.

### 3.2. Forest floor emissions

Highest emissions from forest floor were measured in spring and autumn. Main emitted compounds were monoterpenes (Table 1). Isoprene emissions were small compared to the emissions from Siikaneva fen. Highest monoterpene emissions were measured in spring after the snow had melted (Fig. 3). Emissions dropped in the summer and increased again in autumn. The sum of the measured monoterpene emission rates varied from below the detection limit to  $373 \mu\text{g m}^{-2} \text{h}^{-1}$ . The most abundantly emitted monoterpene was  $\alpha$ -pinene followed by  $\Delta^3$ -carene, camphene, limonene and  $\beta$ -pinene. Emissions were found to increase in autumn also in the study by Janson et al. (1993), conducted in a Scots pine forests in Sweden. In those measurements emission rates varied between 2.6 and  $232 \mu\text{g m}^{-2} \text{h}^{-1}$ . In the study by Hayward et al. (2001) average monoterpene emissions from the soil of a Sitka spruce forest in UK was  $34 \mu\text{g m}^{-2} \text{h}^{-1}$ . The measurements of Hayward et al. (2001) were conducted in the middle of summer, which may explain the relatively low monoterpene emissions as the emission rates were observed to be lower in the middle of the summer also in Hyytiälä.

In Hyytiälä, forest floor emissions were not found to be temperature dependent as in a Sitka spruce forest in UK, where measurements were conducted on three summer days (Hayward et al., 2001). Seasonal factors were observed to have greater effect here. However, daily or seasonal emissions might still be temperature dependent.

Warneke et al. (1999) suggested that the highest VOC emission rates by litter are observed at the beginning of autumn and in late spring. Based on the observed seasonal variation, the probable source of the emissions in Hyytiälä is decaying needle

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litter. There have been suggestions (Janson et al., 1993) that fine roots are a source for forest floor emissions. However, in the experiments where emissions originating from different layers of the soil of a Sitka spruce forest in UK were determined by Hayward et al. (2001), the emissions were found to be originating from the surface litter.

Subsurface parts of the trees were found to emit significant quantities of monoterpenes only if disturbed, damaged or exposed to the atmosphere.

Forest floor emissions of terpenes were compared to the emissions of Scots pine canopy measured by Hakola et al. (2005) using branch chambers. The measured emissions were up-scaled to canopy by assuming a needle biomass density of  $300 \text{ g(dw) m}^{-2}$  (Fig. 4). In summer Scots pine emissions were much higher than the forest floor emissions, but in spring and autumn they were at same level and sometimes even higher forest floor emission was observed. This implies that in spring and autumn monoterpenes emitted from the forest floor can be a significant source for these compounds into the atmosphere. Springtime emissions from the forest floor are quite high even when compared to the summertime emissions from the Scots pine canopy. This is intriguing as terpenes are assumed to participate in the formation or growth processes of secondary organic aerosols and the maximum in new particle formation event frequency is observed during springtime in Northern European boreal regions (Mäkelä et al., 2000).

In 2005 when more sensitive SIM method was used to analyze the VOC samples, chloroform emission from forest floor was detected on all measurement days, as shown in Fig. 5, except for the collar 2 on the first two days, when the collar was still covered with snow. Daily average emission rates varied between  $400$  and  $800 \text{ ng m}^{-2} \text{ h}^{-1}$  for the collar 1 and between  $100$  and  $370 \text{ ng m}^{-2} \text{ h}^{-1}$  for the collar 2. Emissions started after the snow had melted in April and the emission rate remained at the same level also in May and June. This implies that the main chloroform source is not the same as for the terpenes. There are lots of hypotheses on how the chloroform is formed in the soil. Both biotic and abiotic processes have been suggested (Laternus et al., 2005). However, both formation and degradation processes of chloroform in forest soils and

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the role of the forest as a sink and/or source of chloroform are still unclear.

Hoekstra et al. (2001) found in their enclosure measurements in Netherlands that wood chip area and Douglas fir forest emit significant amounts of chloroform (up to  $1000 \text{ ng m}^{-2} \text{ h}^{-1}$ ), but pine forest soil emits only  $18\text{--}19 \text{ ng m}^{-2} \text{ h}^{-1}$ . Much higher emissions were found in this study. Haselmann et al. (2000) studied soil air at different soil layers at a Danish spruce forest site and the results indicated that main source of chloroform was biogenic formation in the upper soil layer. Flux calculated from the concentration gradients in the soil was  $2.6\text{--}160 \text{ ng m}^{-2} \text{ h}^{-1}$ , which is lower than the emissions observed in Hyytiälä. Even by using this lower flux Haselmann et al. (2000) estimated that emissions from the northern temperate forests ( $4.9 \text{ Gg}$ ) may be an important contributor to the atmospheric chloroform burden. However, Laturus et al. (2002) estimated that northern temperate forests are only a minor source globally. By using the average emission rate measured in Hyytiälä ( $450 \text{ ng m}^{-2} \text{ h}^{-1}$ ), and the area of boreal forests ( $1.6 \times 10^7 \text{ km}^2$ ) by Archibold (1995), the annual average emission from the boreal forests would be  $48 \text{ Gg}$  ( $10\text{--}195 \text{ Gg}$ ). This is at the same range as the global anthropogenic emissions, as estimated by Laturus et al. (2002). Dimmer et al. (2001) measured halocarbon emissions from Irish peatland sites. Median of the measured chloroform emission rates was  $525 \text{ ng m}^{-2} \text{ h}^{-1}$ . Emissions of chloroform have also been measured from the rice fields in China (Khalil et al., 1998), where seasonally averaged emissions varied from  $600$  to  $4400 \text{ ng m}^{-2} \text{ h}^{-1}$ . In Irish peatland, emissions were at the same level as in the Scots pine forest in this study and in rice fields emissions were little higher.

Difference in the emissions of chloroform between the two collars is quite high, even though they are spatially close to each other ( $25 \text{ m}$  apart from each other). Substantial variations in chloroform and other halocarbon emissions between forest floor positions located just a few meters apart have also been seen by Dimmer et al. (2001) and Hoekstra et al. (2001). Dimmer et al. (2001) explained the variations by the very local production of halocarbons by wood-rotting fungi and other microorganisms.

No emissions of other halogenated hydrocarbons were detected. In April and May

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when monoterpene emissions were highest some emissions of sesquiterpenes ( $\beta$ -caryophyllene) were detected, with highest emission rates being  $0.8 \mu\text{g m}^{-2} \text{h}^{-2}$ . In addition to the terpenes and chloroform also small emissions of ethene, propane, propene, 2-methylpropene, cis-2-butene, pentane, hexane and heptane were found (Table 1).

Snow covered forest floor did not emit significant amounts any of studied compounds. As shown in Table 1 only small emissions of propane, propene, 2-methylpropene, chloroform and monoterpenes were detected.

#### 4. Conclusions

Isoprene is the dominant non-methane hydrocarbon emitted from the wetland growing *Sphagnum* moss. Other compounds with detectable emissions were propane, pentane, hexane, butane, ethene, propene, 1-butene and 2-methylpropene. No emissions of monoterpenes or halogenated hydrocarbons from the wetland were detected. The mean isoprene emission potential was  $224 \mu\text{g m}^{-2} \text{h}^{-1}$ , with highest emission potentials measured in August. The emission potential obtained here is lower than the emission potentials published earlier and most likely at least partly caused by cloudy and cold weather during the measurements. The *Sphagnum* moss was found to be the main source of the isoprene from the wetland.

Highest VOC emissions from forest floor were measured in spring and autumn. Main emitted compounds were monoterpenes. Emission rate of the sum of monoterpenes varied between 0 and  $373 \mu\text{g m}^{-2} \text{h}^{-1}$ . The most abundantly emitted monoterpene was  $\alpha$ -pinene followed by  $\Delta^3$ -carene, camphene, limonene and  $\beta$ -pinene. Isoprene emissions were small compared to the emission measured from Siikaneva fen. Compared to the monoterpene emissions from the Scots pine canopy, the forest floor was found to be a significant source of monoterpenes in spring and autumn.

In 2005 when more sensitive SIM method was used, chloroform emission was detected on all measurement days from forest floor. Emissions started after the snow

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had melted in April and the emission rate remained at same level also in May and June. This implies that main chloroform source is not the same as for the terpenes.

Small emissions ( $<2 \mu\text{g m}^{-2} \text{h}^{-1}$ ) of ethene, propane, propene, 2-methylpropene, cis-2-butene, pentane, hexane and heptane from the forest floor were detected.

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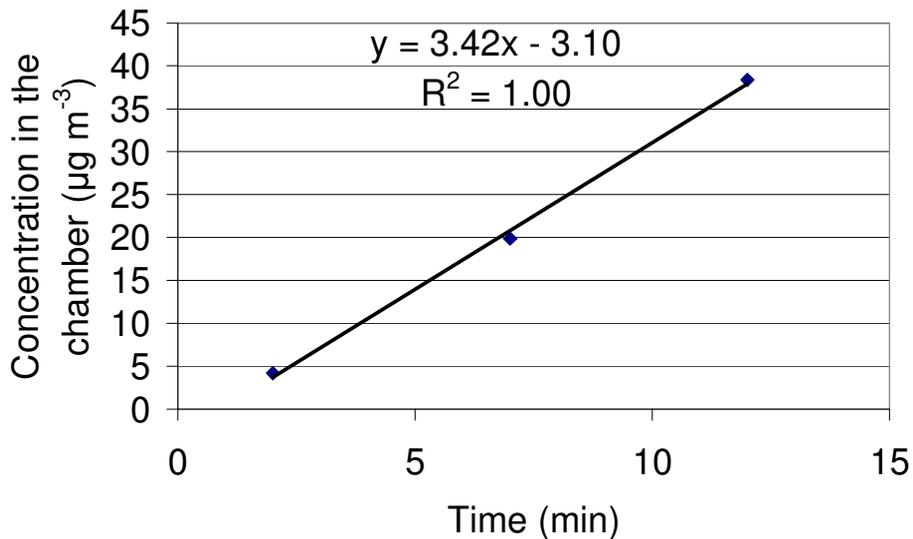
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**Table 1.** Measured emission rates on Siikaneva fen and forest floor in Hyytiälä in spring, summer and autumn of 2004.

( $\mu\text{g m}^{-2} \text{h}^{-1}$ )	Wetland Siikaneva-04	Snow Hyytiälä-04	Forest floor Hyytiälä-04	Forest floor Hyytiälä-05
Ethene	0–1.7	n.d.	0–1.8	–
Propane	0–0.42	0–0.06	0–1.0	–
Propene	0–0.37	0–0.06	0–0.5	–
1-butene	0–0.18	n.d.	n.d.	–
2-methylpropene	0–0.25	0–0.04	0–0.09	–
cis-2-butene	n.d.	n.d.	0–0.05	–
Pentane	0–0.43	n.d.	0–0.4	–
Butane	0–0.13	n.d.	n.d.	–
Hexane	0–0.11	n.d.	0.04	–
Isoprene	1.3–53	n.d.	0–1.9	–
Heptane	n.d.	n.d.	0–0.17	–
Chloroform	n.d.	0.01–0.03	0–1.1	0–1.2
a-Pinene	n.d.	0–0.09	0.07–161	0–123
Camphene	n.d.	0–0.1	0–27.2	0–6.7
Sabinene	n.d.	n.d.	0–2.2	0–0.6
b-Pinene	n.d.	0–0.02	0–16.8	0–2.4
3-Carene	n.d.	0–0.03	0–152	0–51.8
Limonene	n.d.	n.d.	0–13.4	0–5.8
1,8-Cineol	n.d.	n.d.	0–2.3	n.d.
$\beta$ -Caryophyllene	n.d.	n.d.	0–0.80	0–0.1

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**Fig. 1.** Concentration change of isoprene in the chamber during a closure of the chamber on Siikaneva fen.

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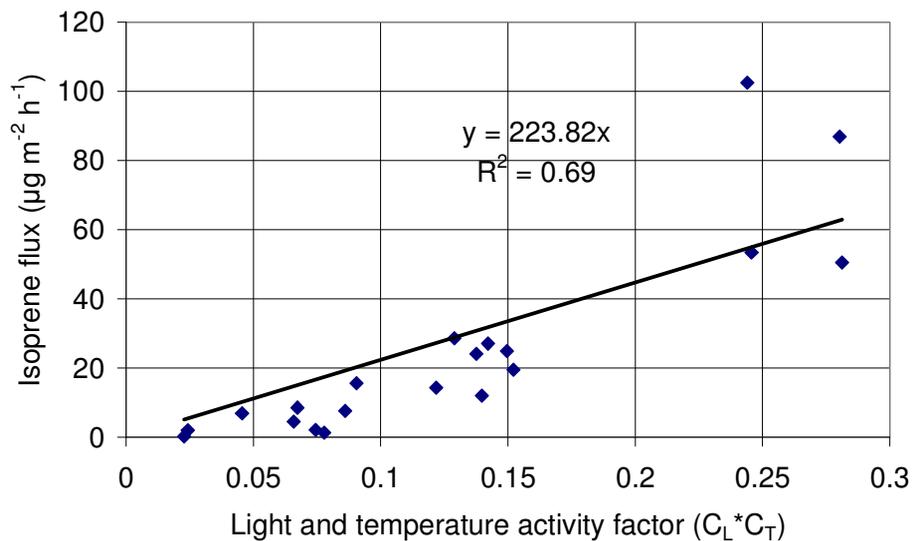
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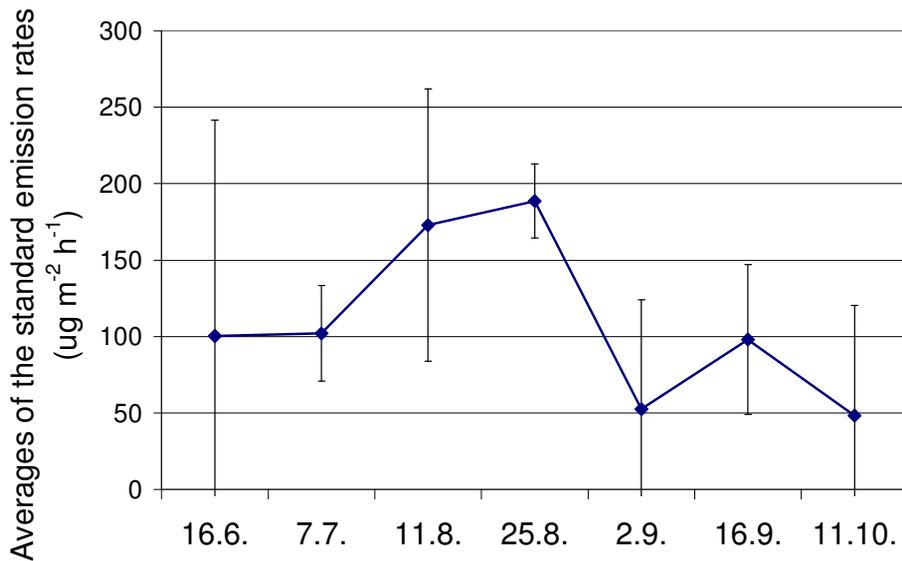
**Fig. 2.** Light and temperature dependence of measured isoprene emission rates.

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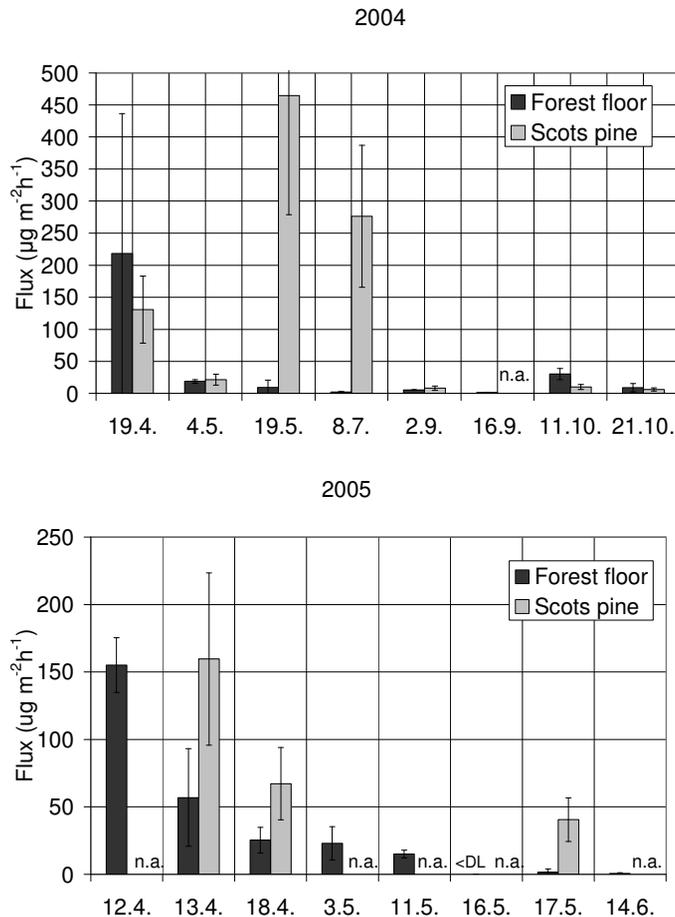
**Fig. 3.** Standard ( $30^{\circ}\text{C}$  and  $1000 \mu\text{mol m}^{-2} \text{h}^{-1}$ ) emission potentials of the isoprene on Siikaneva fen in 2004. (Error bars= $2 \times$  standard error of mean).

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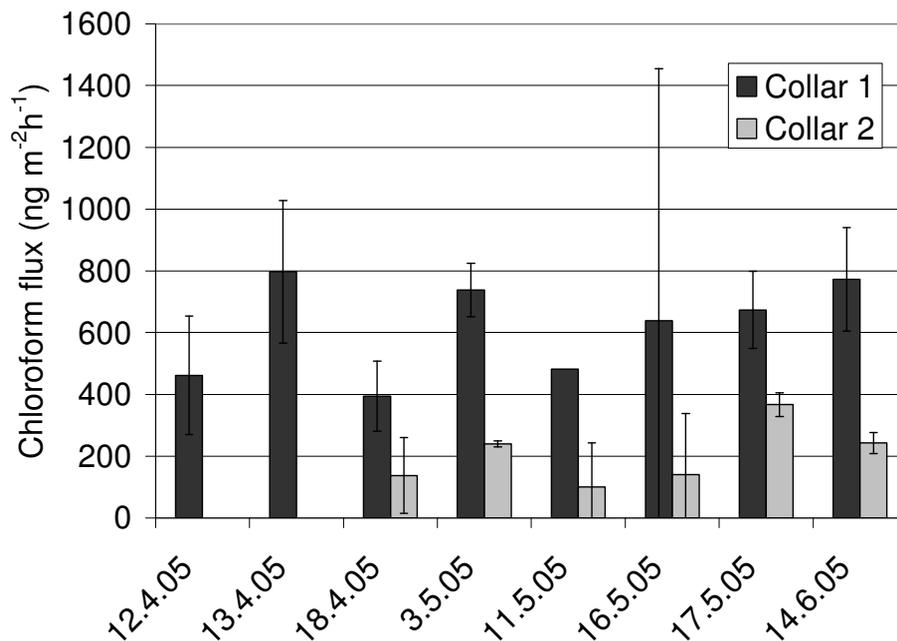


**Fig. 4.** Sum of the measured emission rates of the terpenes from the forest floor and Scots pine (for biomass density  $300\text{ g m}^{-2}$ ) in Hyytiälä in 2004 and 2005. Data for Scots pine emissions on 16 September in 2004 was missing and in 2005 data was available only for 13 and 18 April and for 17 May.

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**Fig. 5.** Average and standard deviation of the measured emission rates of chloroform on different days from two different collars from the forest floor in Hyttiälä in 2005. On 12 and 13 April collar 2 was still covered with snow and no emissions were detected.

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