Biogeosciences

C$_2$-C$_{10}$ hydrocarbon emissions from a boreal wetland and forest floor

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Abstract. Emissions of various C$_2$-C$_{10}$ hydrocarbons (VOCs) and halogenated hydrocarbons (VHOCs) from a boreal wetland and a Scots pine forest floor in south-western Finland were measured by the static chamber technique. Isoprene was the main non-methane hydrocarbon emitted by the wetland, but small emissions of ethene, propane, propene, 1-butene, 2-methylpropene, butane, pentane and hexane were also detected. The isoprene emission from the wetland was observed to follow the commonly-used isoprene emission algorithm. The mean emission potential of isoprene was $224\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$ for the whole season. This is lower than the emission potentials published earlier; that is probably at least partly due to the cold and cloudy weather during the measurements. No emissions were detected of monoterpenes or halogenated hydrocarbons from the wetland. The highest hydrocarbon emissions from the Scots pine forest floor were measured in spring and autumn. However, only a few measurements were conducted during summer. The main compounds emitted were monoterpenes. Isoprene emissions were negligible. The total monoterpene emission rates varied from zero to $373\,\mu\mathrm{g\,m^{-2}\,h^{-1}}$. The results indicated that decaying plant litter may be the source for these emissions. Small emissions of chloroform (100–$800\,\mathrm{ng\,m^{-2}\,h^{-1}}$), ethene, propane, propene, 2-methylpropene, cis-2-butene, pentane, hexane and heptane were detected. Comparison with Scots pine emissions showed that the forest floor may be an important monoterpene source, especially in spring.

1 Introduction

C$_2$-C$_{10}$ hydrocarbons (VOCs) have an impact on atmospheric chemistry in many ways. In the atmosphere they are oxidized by hydroxyl radicals, ozone and nitrate radicals, and they contribute to the production of tropospheric ozone (Atkinson, 2000). In their reactions carbonyls and acids are produced, and therefore they may make a contribution to the organic content and acidity of precipitation. One important aspect is that the reaction products of VOCs may also take part in formation and growth of new particles, with possible consequents for climate (Griffin et al., 1999; Hoffmann et al., 1997). Globally, biogenic sources (e.g., trees and other vegetation) (Guenther et al., 1995) are the main source of VOCs for the atmosphere. However, these sources are not well characterized. Halogenated hydrocarbons (VHOCs) with long atmospheric lifetimes contribute to the destruction of stratospheric ozone. Some of the VOCs and VHOCs are also harmful or toxic to both humans and the environment.

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 this zone. While the VOC emissions from boreal forest ecosystems have been studied quite intensively (e.g. Janson 1993, Hakola et al., 1998, 2001, 2003, 2006; Rinne et al., 2000; Janson and De Serves, 2001; Tarvainen at al., 2005), data on the wetlands are scarce. Janson et al. (1999), Jansson and De Serves (1998) and Haapanala et al. (2006) have shown that the boreal wetlands are a significant source of isoprene. In a study by Rinnan et al. (2004) various VOCs, emitted from wetland microcosm samples taken from a wetland in Finland, were identified, but not quantified.

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 to be small compared to the canopy

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Table 1. The environmental conditions occurring during the sampling; Average local air temperature (Air T) and relative humidity (AirRH), soil temperature at depth of 20 cm (SoilT-20cm) and 5 cm (SoilT-5cm) below the surface and average photosynthetically active radiation (PAR).

	AirT (K)	AirRH(%)	SoilT -20 cm (K)	SoilT -5 cm (K)	PAR (μmol*m^{-2}h^{-1})
16/6/2004	284	86	283	286	979
7/7/2004	288	85	286	290	691
11/8/2004	291	78	290	291	588
25/8/2004	288	53	287	285	1409
2/9/2004	286	100	287	287	394
16/9/2004	282	69	285	284	724
11/10/2004	276	61	282	276	760
18/8/2005	298	49	–	–	1135

emissions. This has also been demonstrated in the studies by Janson (1993), Janson et al. (1999), and Hayward et al. (2001), who found monoterpene emissions from the forest floor in summer to be insignificant compared to the emissions from trees. However, during other seasons the forest floor may have an important role. Isidorov et al. (2003, 2005) have found in their laboratory studies that decomposing leaf litter emits several different VOCs. These emissions would occur during autumn and again in spring after the snow has melted and the ground thawed out.

Wetlands and the forest floor may also be a significant source for halogenated hydrocarbons that have been observed to be emitted e.g. by wetlands and the 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 the Netherlands (Haselmann et al., 2000 and Hoekstra et al., 2001). Soil emissions have been estimated to be major contributor to the atmospheric chloroform burden (Laturnus et al., 2002). However, due to the lack of emission data, estimates are still highly uncertain. To our knowledge data for the boreal zone are very limited.

The purpose of this study was to identify the emissions of various different C_2-C_{10} hydrocarbons and halogenated hydrocarbons from a boreal wetland and forest floor, and to estimate their importance and fluxes to the atmosphere. Earlier studies conducted on boreal wetlands have concentrated on isoprene only and have ignored emissions of other VOCs (Haapanala et al., 2006; Janson et al., 1999, and Janson and De Serves, 1998). In this study the fluxes of other hydrocarbons were also quantified. As already mentioned, there are some earlier studies conducted on forest floor emissions in summer, but other seasons may be more important. Spring is of special interest at the measurement location, since VOCs may be precursors of secondary organic aerosols and most of the new particle formation events occur in spring (Mäkelä et al., 2000) This study is therefore concentrated on spring and autumn with the emphasis on evaluating the relative importance of the ground emissions to the emissions of the Scots

pines (the main local trees). The boreal zone may also be a significant source for halogenated hydrocarbons, but no data exist to shed light on this question. For this reason the present study is also aimed at studying the emissions of halogenated hydrocarbons.

2 Materials and methods

The forest floor measurements were conducted at the Hyytiälä SMEAR II measurement station (61°51′ N, 24°17′ E, 180 m a.s.l.) in the south boreal zone of southern Finland, while the wetland measurements were carried out at the Siikaneva fen located a few kilometres west of 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 the 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 schreberi, Hylocomium splendens*). The soil type is Haplic Podzol. In addition to mosses, both plots contained some shrubs and some litter from the surrounding trees and other vegetation. Siikaneva is an open aapa fen and its vegetation is dominated by mosses (*Sphagnum balticum, S. papillosum, S. magellanicum* and *S. majus*), sedges (*Carex rostrata, C. limosa* and *Eriophorum vaginatum*) and Rannoch-rush (*Scheuchzeria palustris*). The fen is surrounded by coniferous forests. The plots at Siikaneva contained both mosses and sedges. 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 the 2004 data, one additional measurement was conducted at Siikaneva on the 18 August 2005. Details of the environmental conditions occurring during the sampling are shown in Table 1.

According to the statistics of the Finnish Meteorological Institute, April 2004 was very dry, with precipitation amounts far below the long-term average. Summer 2004 was exceptionally rainy, with the record high precipitation amounts in southern and central Finland in July. May, June and July were also cloudier than the long-term average, and September was again quite rainy. Spring 2005 was a little colder and drier than the long-term average.

Measurements were conducted using the static chamber technique on five different stainless steel collars (60 cm × 60 cm) at Siikaneva and on two different collars at Hyytiälä. The collars were installed randomly on the ground about six months 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 dimensions of 60 cm × 60 cm × 25 cm. One chamber was made of stainless steel frames and the other of aluminum frames. Both chambers were covered inside with transparent Teflon film and therefore had transparent walls and roof. A Teflon-membrane pump was used to circulate the air in the chamber.

The emission rate was determined from the increase in 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. The time intervals between the three samples were varied from 5 minutes to 50 min in order to find the optimum sampling time. In most cases, 10 min was found to be the best compromise. If the linearity of the concentration increase was poor (i.e., the correlation coefficient (R^2) between concentration and time was less than 0.8), the results were not used in flux calculations. Because the sampling interval for some of the samples at the beginning of the measurement period in 2004 was too long, emissions had to be calculated using only the first two samples in these cases.

Some of the VOCs, such as the monoterpenes, are very reactive towards ozone, which can pose problems in 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 no ozone removal techniques were used in this study, ozone should not be a problem. In 2005, comparisons were conducted with a dynamic chamber system, where ozone was removed with MnO_2 coated copper nets. The VOC emissions measured by these two systems were at same level, and this gave further confirmation that ozone was not a problem in the static chamber measurements.

The 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 a depth of 10 cm was only 0.2°C. In our study the increase in air temperature was found to be significant (>2°C) only on sunny and warm days. As the summer

of 2004 was exceptional cold and rainy this was not a serious problem for most of the measurements in this study.

The VOC and VHOC samples from the chambers were taken using Tenax TA-Carbopack B adsorbent tubes and 0.85 L stainless steel canisters. For adsorbent samples, critical orifices with membrane pumps were used. Flow rates were ca. 50 ml min^{-1}. From the adsorbent tubes C_5-C_{10} 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 the more sensitive SIM (selective ion monitoring) mode was used. The detection limits therefore in 2005 were lower than in 2004. Lighter C_2-C_6 and halogenated hydrocarbons were analysed from the canisters using a gas chromatograph (HP-6890) with an Al_2O_3/KCl PLOT column. After the column, the sample flow was split into two different detectors: C_2-C_7 hydrocarbons were detected using a flame ionization detector (FID) and a halogenated hydrocarbon (chloromethane) with an electron capture detector (ECD). Before the analysis, water and CO_2 were removed using a K_2CO_3/NaOH drier. Subsequently the sample (c.a. 500 ml) was concentrated using two liquid nitrogen traps. For adsorbent samples, a five-point calibration was performed using liquid standards in a methanol solution. For the canister samples, gas-phase standards from the NPL (National Physical Laboratory, UK) for VOCs and from NOAA (National Oceanic and Atmospheric Administration, USA) for VHOCs were used.

A blank test was conducted by covering a collar with Teflon film and placing the measurement chamber on it. Three samples were taken from the chamber at 10 minutes intervals; similar sampling lines and pumps were used as for the real samples. The concentrations in the chamber did not change during the enclosure and no production or degradation of measured compounds was detected.

Isoprene emissions from vegetation are light- and temperature-dependent. This dependence can be described by the algorithms presented by Guenther et al. (1993) and Guenther (1997). The standard emission potential can be obtained by linearly fitting the emission rates to the light and temperature activity factors ($C_T * C_L$) of the isoprene emission algorithm.
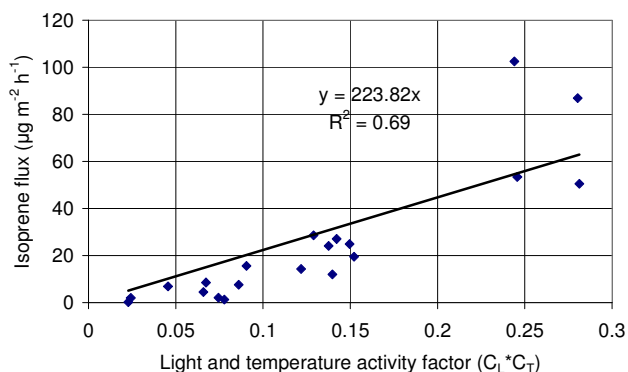
Fig. 1. Light and temperature dependence of measured isoprene emission rates on Siikaneva fen.

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

3   Results and discussion

3.1   Wetland emissions

3.1.1   VOC emissions from the Siikaneva fen

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

The standard emission potential of the isoprene emission was $224\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$ (Fig. 1). The coefficient of correlation between measured emission rates and the light and temperature activity factor (C_T*C_L) of the Guenther algorithm was 0.69 (Fig. 1). While temperature and PAR explain much of the variation, other factors can also have an effect. For example, the seasonal growth pattern and water content of the moss or other vegetation may explain part of the variation (Janson and De Serves, 1998). Standard (T=$30°C$ and PAR=$1000\,\mu\text{mol}\,\text{m}^{-2}\,\text{s}^{-1}$) emission potentials for isoprene were calculated for each measurement separately using the isoprene emission algorithm. Daily average values are shown in Fig. 2. The results indicate that the highest standard emission potentials are measured in August. However, more measurements are needed to verify this conclusion.

In a VOC flux study by the REA technique at Siikaneva in 2004 and 2005, the average standard emission potential for isoprene was found to be $680\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$ (Haapanala et al., 2006), which is several times higher than that found in this study. However, Haapanala et al. (2006) observed that for low C_T*C_L values (<0.2), the emission potential was lower, only $330\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$. This value is closer to the emission potential obtained in this study, in which the C_T*C_L values were low. Another possible reason for dif-
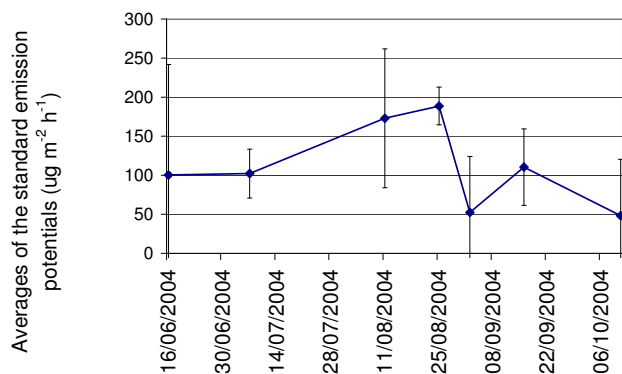
ferences in the measured emissions is that the REA technique measures flux from much larger area than the chamber technique. If the footprint of the REA measurements is not totally homogeneous, comparison with the small plots from the area may give different results. However, Janson and De Serves (1998) also found higher emission potentials ($700\pm400\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$) using the chamber technique on *Sphagnum* fens in Sweden and Finland in June–August 1997, but their measurements were also conducted in warm and sunny conditions.

No clear emissions of monoterpenes, aromatic hydrocarbons or other larger volatile organic compounds ($>C_5$) were detected, although Rinnan et al. (2004) found the emission of 45 different C_4-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 they themselves raised the question of possible contamination of the microcosms during transportation.

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. The standard emission potential of isoprene from the plot containing mosses only was $127\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$, which is close to the average value for the other plots ($110\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$) on same day. From the plot from which both green mosses and sedges were removed, almost no emissions were detected (emission potential $<1\,\mu\text{g}\,\text{m}^{-2}\,\text{h}^{-1}$). This indicates that the *Sphagnum* moss is the main source of the isoprene emitted by the fen.

3.1.2   VHOC emissions from the Siikaneva fen

Despite the special efforts made, no emissions of halogenated hydrocarbons were detected. In the studies of Dimmer et al. (2001), significant emissions of CH_3Cl, CH_3Br, CH_3I and $CHCl_3$ were found to be emitted from wetlands and the forest floor in Ireland, while Varner et al. (1999) have

Table 2. Range of the measured emission rates on the Siikaneva fen and the forest floor at Hyytiälä in spring, summer and autumn of 2004 and in spring and early summer 2005.

$(\mu g\,m^{-2}\,h^{-1})$	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

reported emissions of CH_3Cl and CH_3Br from two wetlands in the Northeastern United States, both dominated by *Sphagnum* and *Carex* species. One reason for the lack of emissions may be that Siikaneva is located far away from sea areas, which are sources of chlorine. In addition to this, the salinity of the closest sea (the Baltic Sea) is lower than that of most major seas in the world. Foltescu et al. (2005) for example have shown that the average seasalt deposition flux in particles is much higher in Ireland, where Dimmer et al. (2001) conducted their measurements, than in Finland.

3.2 Forest floor emissions

3.2.1 VOC emissions from the forest floor

The highest emissions from the forest floor were measured in spring and autumn. The main emitted compounds were monoterpenes (Table 2). The isoprene emissions were small compared to its emissions from the Siikaneva fen. The highest monoterpene emissions were measured in spring after the snow had melted at the beginning of April (Fig. 3). Emissions dropped in the summer and increased again in the autumn. However, more measurements are needed to verify these results. The sum of the measured monoterpene emission rates varied from below the detection limit to $373\,\mu g\,m^{-2}\,h^{-1}$. The most abundantly-emitted monoterpene was α-pinene followed by Δ^3-carene, camphene, limonene and β-pinene. Emissions were also found to increase in au-

tumn in the study by Janson et al. (1993), conducted in Scots pine forests in Sweden. In those measurements, emission rates varied between 2.6 and $232\,\mu g\,m^{-2}\,h^{-1}$. In the study by Hayward et al. (2001), the average monoterpene emissions from the soil of a Sitka spruce forest in the UK were $34\,\mu g\,m^{-2}\,h^{-1}$. The measurements of Hayward et al. (2001) were conducted in the middle of summer, which may explain the relatively low monoterpene emissions: lower emission rates were also observed in the middle of the summer in Hyytiälä.

Warneke et al. (1999) suggested that the highest VOC emission rates by litter are observed at the beginning of autumn and in late spring. There have also been suggestions (Janson et al., 1993) that fine roots are a source for forest floor emissions. However, in the experiments by Hayward et al. (2001), in which emissions originating from different layers of the soil of a Sitka spruce forest in UK were determined, 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. The high emissions in spring and autumn indicated that litter may also be the source of monoterpenes in this study. Monoterpene emissions from living vegetation are known to be temperature dependent (Guenther et al., 1993), so that the lack of temperature-dependence also gave support to the hypothesis that litter is the main source. In the Sitka spruce forest in
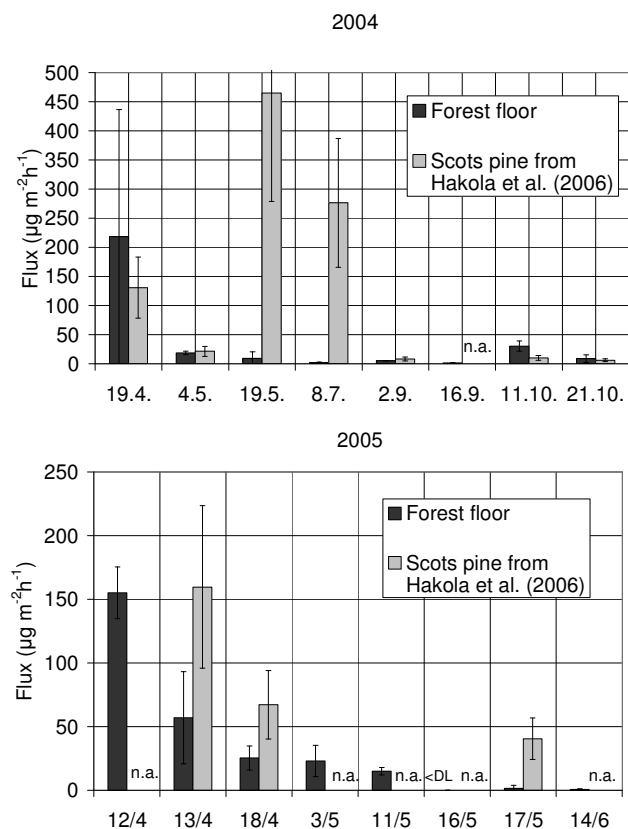
Fig. 3. Sum of the measured emission rates of the terpenes from the forest floor and Scots pine (for biomass density $300 \, g \, m^{-2}$) at Hyytiälä in 2004 and 2005. The Scots pine results are from the study of Hakola et al. (2006). Data for Scots pine emissions on 16th of September 2004 were missing and in 2005 data were only available for 13 and 18 April and for 17 May. (Bars=daily average and error bars=standard deviations between the samples)

the UK, where measurements were conducted on three summer days (Hayward et al., 2001), forest floor emissions were found to be temperature-dependent, but in this study seasonal factors were observed to have a greater effect. However, daily or seasonal emissions might still be temperature-dependent.

The forest floor emissions of terpenes were compared to the emissions of a Scots pine canopy measured by Hakola et al. (2006) using branch chambers. The measured emissions were up-scaled to the canopy by assuming a needle biomass density of $300 \, g(dw) \, m^{-2}$ (Fig. 3). In summer, the Scots pine emissions were much higher than those of forest floor, but in spring and autumn the emissions were at the same level; 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 of these compounds for 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 in-
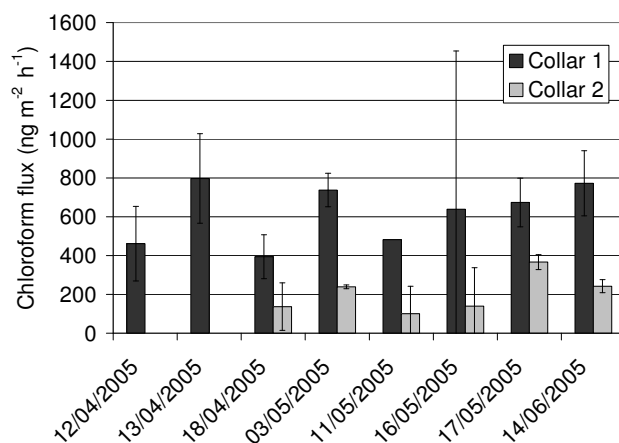

Fig. 4. Daily average (bars) and standard deviation (error bars) of the measured emission rates of chloroform on different days from two different collars from the forest floor at Hyytiälä in 2005. On 12 and 13 April collar 2 was still covered with snow and no emissions were detected.

triguing, as terpenes are believed to participate in the formation or growth processes of secondary organic aerosols, and the maximum in new particle formation event frequency in Northern European boreal regions is observed during springtime (Mäkelä et al., 2000).

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

None of the studied compounds were emitted in significant amounts from the snow-covered forest floor. As shown in Table 2, only small emissions of propane, propene, 2-methylpropene, chloroform and monoterpenes were detected.

3.2.2 VHOC emissions from the forest floor

In 2005 when more sensitive selected ion monitoring (SIM) method was used to analyze the VHOC samples, chloroform emission from the forest floor was detected on all measurement days, as shown in Fig. 4, except for collar 2 on the first two days, when the collar was still covered with snow. Daily average emission rates varied between 400 and $800 \, ng \, m^{-2} \, h^{-1}$ for collar 1 and between 100 and $370 \, ng \, m^{-2} \, h^{-1}$ for collar 2. Emissions started after the snow had melted in April, and the emission rate also remained at the same level in May and June (Fig. 4). This implies that the main chloroform source is not the same as for the terpenes. However, Haselmann et al. (2002) found that the highest chloroform concentrations in the soil air of a Danish spruce forest are measured in spring and autumn. There are

many hypotheses as to how the chloroform is formed in the soil. Both biotic and abiotic processes have been suggested. These possible formation processes have been recently reviewed by Laturnus et al. (2005). However, both the formation and degradation processes of chloroform in forest soils and the role of the forest as a sink and/or source of chloroform are still unclear. No emissions of other halogenated hydrocarbons were detected.

Hoekstra et al. (2001) found in their enclosure measurements in the Netherlands that a wood chip area and Douglas fir forest emit significant amounts of chloroform (up to $1000\,\mathrm{ng\,m^{-2}\,h^{-1}}$), but that pine forest soil emits only 18–$19\,\mathrm{ng\,m^{-2}\,h^{-1}}$. Much higher emissions were found in this study. Haselmann et al. (2000) studied soil air from different soil layers at a Danish spruce forest site; the results indicated that the main source of chloroform was biogenic formation in the upper soil layer. The flux calculated from the concentration gradients in the soil was 2.6–$160\,\mathrm{ng\,m^{-2}\,h^{-1}}$, which is lower than the emissions observed at Hyytiälä. Even using this lower flux value Haselmann et al. (2000) estimated that emissions from the northern temperate forests (4.9 Gg) may be an important contributor to the atmospheric chloroform burden. However, Laturnus et al. (2002) estimated that the northern temperate forests are only a minor source globally. Using the average emission rate measured at Hyytiälä ($450\,\mathrm{ng\,m^{-2}\,h^{-1}}$), and the area of boreal forests ($1.6\times10^{7}\,\mathrm{km^2}$) as given by Archibold (1995), the annual average emission from the boreal forests would be 48 Gg (10–195 Gg). This is in the same range as global anthropogenic emissions, as estimated by Laturnus et al. (2002). However, more measurements at different locations and microsites are needed to really estimate the magnitude of the emissions. This is only intended to show that boreal forests might be an important chloroform source. Dimmer et al. (2001) measured halocarbon emissions from Irish peatland sites. The median of the measured chloroform emission rates was $525\,\mathrm{ng\,m^{-2}\,h^{-1}}$. 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 $4400\,\mathrm{ng\,m^{-2}\,h^{-1}}$. In the Irish peatland, emissions were at the same level as in the Scots pine forest in this study, while rice-field emissions were a little higher.

The difference between the two collars in their emissions of chloroform is quite high, even though they are spatially close to each other (25 m apart). Substantial variations in chloroform and other halocarbon emissions between forest floor positions just a few metress apart have also been observed 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. This also shows that more measurements are needed to better describe the chloroform emissions from the boreal forest floor.

4 Conclusions

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

The highest VOC emissions from the forest floor were measured in spring and autumn. However, more measurements are needed to verify these results. The main compounds emitted were monoterpenes. The emission rate of the sum of the monoterpenes varied between 0 and $373\,\mathrm{\mu g\,m^{-2}\,h^{-1}}$. The most abundantly-emitted monoterpene was α-pinene, followed by Δ^3-carene, camphene, limonene and β-pinene. Isoprene emissions were small compared to the emission measured from the 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 both spring and autumn. Small emissions ($<2\,\mathrm{\mu g\,m^{-2}\,h^{-1}}$) of ethene, propane, propene, 2-methylpropene, cis-2-butene, pentane, hexane and heptane from the forest floor were also detected.

In 2005, when the more sensitive SIM method was used, chloroform emission was detected from the forest floor on all measurement days. Emissions started after the snow had melted in April and the emission rate also remained at same level in May and June. This implies that the main chloroform source is not the same as for the terpenes.

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