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Non-methane volatile organic compound flux from a subarctic mire in Northern Sweden

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ABSTRACT

Biogenic NMVOCs are mainly formed by plants and microorganisms. They have strong impact on the local atmospheric chemistry when emitted to the atmosphere. The objective of this study was to determine if there are significant emissions of non-methane volatile organic compounds (NMVOCs) from a subarctic mire in northern Sweden. Subarctic peatlands in discontinuous permafrost regions are undergoing substantial environmental changes due to their high sensitivity to climate warming and there is need for including NMVOCs in the overall carbon budget. Automatic and manual chamber measurements were used to estimate NMVOC fluxes from three dominating subhabitats on the mire during three growing seasons. Emission rates varied and were related to plant species distribution and seasonal net ecosystem exchange of carbon dioxide. The highest fluxes were observed from wetter sites dominated by *Eriophorum* and *Sphagnum* spp. Total NMVOC emissions from the mire (∼17 ha) is estimated to consist of ∼150 kgC during a growing season with 150 d. NMVOC fluxes can account for ∼5% of total net carbon exchange (−3177 kgC) at the mire during the same period. NMVOC emissions are therefore a significant component in a local carbon budget for peatlands.

1. Introduction

The diverse group of atmospheric trace gases called non-methane volatile organic compounds (NMVOCs) includes isoprenoids, alkanes, alkenes, carbonyls, alcohols, esters, ethers and acids (Kesselmeier and Staudt, 1999). They are emitted to the atmosphere from both anthropogenic activities and natural processes. Natural emissions represent the largest source (Guenther et al., 1995). Biogenic NMVOCs can be formed by living plants or during microbial degradation of organic matter (Beckmann and Lloyd, 2001; Penuelas and Llusia, 2001; Isidorov and Jdanova, 2002). Suggested functions of NMVOCs for plants include attracting pollinators, repelling pests and export of metabolites. Emissions can also be due to unintentional losses from the organism (Penuelas and Llusia, 2001; Sharkey and Yeh, 2001).

Both anthropogenic and natural NMVOCs play an important role in the global carbon cycle. In the atmosphere, they are oxidized by hydroxyl radicals (OH), ozone and nitrate radicals and contribute to the formation of tropospheric ozone (Kesselmeier and Staudt, 1999; Atkinson, 2000). These volatile compounds are also involved in organic aerosol production affecting particle lifetime in the atmosphere as well as precipitation acidity (Hoffmann et al., 1997; Atkinson, 2000; IPCC, 2001; Kulmala et al., 2004). NMVOCs are thought to indirectly influence atmospheric loading of greenhouse gases such as carbon dioxide (CO_2), carbon monoxide (CO) and methane (CH_4) because of competition for OH radicals (Kesselmeier et al., 2002). CH_4 is also oxidized by OH radicals and thereby a consumption of OH radicals by other volatiles may affect its atmospheric lifetime (Kaplan et al., 2006). Since biogenic NMVOCs are involved in biogeochemical processes at the plant species and ecosystem level, and potentially emitted to the atmosphere, they constitute an important link in the carbon cycle between the atmosphere and biosphere.

At the ecosystem level, biogenic NMVOC emissions may account for a significant amount of the total carbon budget. The global mean emission has been estimated to be approximately 2% of the net primary production (NPP) (Guenther et al., 1995). Extreme environmental conditions such as high temperatures and water stress can substantially increase NMVOC production and release. For example, physiological stress has caused emissions from kudzu (*Pueraria montana*) leaves to be as high as 67% of the carbon fixed in photosynthesis (Sharkey and Loreto, 1993).

Many plant species have been identified in emission inventories for specific volatile compounds and many studies have focused on light and temperature controls (e.g. Penuelas and

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Llusia, 2001; Sharkey and Yeh, 2001; Schnitzler et al., 2002). Tropical and boreal forests have received most of the previous attention regarding NMVOC exchange (Zimmerman et al., 1988; Crutzen et al., 2000; Kesselmeier et al., 2000; Rinne et al., 2000; Janson and de Serves, 2001; Hakola et al., 2003). These regions cover a large spatial area and have large amounts of biomass with plant species that are known emitters. Due to light and temperature controls on NMVOC production and release, the either very long or very intense periods of insolation in tropical and boreal regions implies a potential for globally significant NMVOC emissions.

Other ecosystems have received less attention in terms of natural emissions of low molecular weight carbon trace gases other than CO_2 and CH_4. Previous wetland studies typically focused on boreal wetlands that have been shown to emit significant emissions of isoprene (Klinger et al., 1994; Janson and De Serves, 1998; Janson et al., 1999; Rinnan et al., 2005; Haapanala et al., 2006; Hellén et al., 2006). Studies of total NMVOC emissions from arctic and subarctic wetlands north of the boreal zone seemingly have not been published earlier. Boreal and subarctic wetland ecosystems cover approximately 3.5 million km^2 and could potentially contribute large amounts of volatile organic carbon due to the presence of plant species that are known NMVOC emitters (e.g. *Sphagnum* spp. and *Betula* spp.; Janson et al., 1999; Hakola et al., 2001; Rinnan et al., 2005; Hellén et al., 2006). Microbial decomposition of organic matter has been found to be a source of NMVOCs and, considering the large amounts of partly degraded organic carbon stored in peatlands, this could potentially be another important source (Beckmann and Lloyd, 2001; Isidorov and Jdanova, 2002).

The objective of this study was to investigate if there are significant emissions of NMVOCs from the subarctic mire Stordalen in northern Sweden. To account for both spatial and temporal variability, we studied the three dominating types of subhabitats on the mire during three growing seasons, which enable a discussion of the ecosystem level scale of NMVOC emissions from this type of environment.

2. Methods

2.1. Site description

The study site is the subarctic Stordalen Mire, 10 km southeast of Abisko, in northern Sweden (68°22′N, 19°03′E; Fig. 1). The mean annual temperature at the Abisko Scientific Research Station is −0.7 °C for the period 1913–2003 and the accumulated yearly precipitation for the same period is 304 mm. The 20 yr mean growing season temperature (June 15–August 30) is 10.6 °C and accumulated growing season precipitation is 115 mm. The growing season temperatures for each of the 3 yr (2003–2005) of this study were 12.5, 11.5 and 11.9 °C while accumulated precipitation was 101, 243 and 115 mm at the same location.

The Stordalen Mire is characterized by discontinuous permafrost resulting in variable small-scale surface topography with elevation differences of less than 2 m over short distances. Topographical differences affect the surface hydrology which, in turn, controls moisture and nutrient availability and thereby the formation of subhabitats dominated by different vegetation types and plant species. In this study, we examine three typical subhabitats found on the mire: (i) a dry Palsa dominated by feather mosses, ericaceous and other woody vegetation typical of drained, cold peats; (ii) a wet *Sphagnum* spp. site dominated by *Sphagnum* mosses and characterized by a highly variable water table position and (iii) a wet *Eriophorum angustifolium* site with stable water table. The subhabitats are hereafter designated Palsa, *Sphagnum* and *Eriophorum* sites. Plant species occurrences as well as other environmental characteristics are listed for in Table 1. The total mire area is approximately 17 ha. The Palsa, *Sphagnum* and *Eriophorum* sites constitute 8.3 (49%),

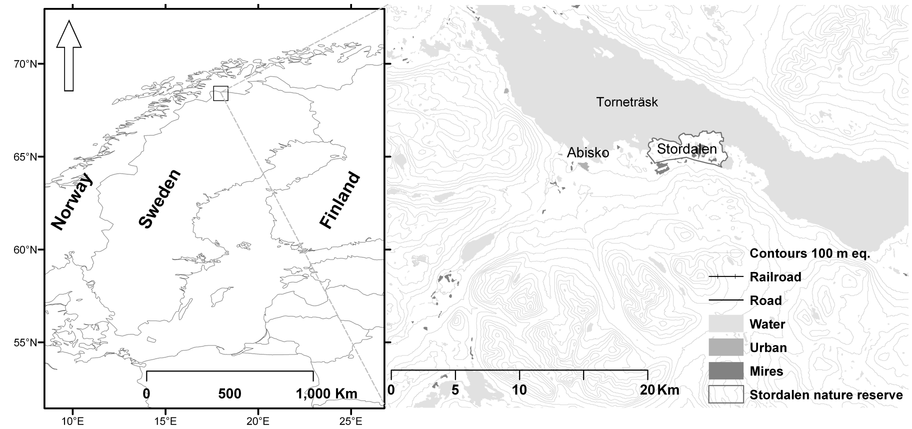

Fig. 1. Field site location in northern Sweden. The study site, Stordalen mire, is located within the Stordalen nature reserve 10 km east of Abisko and the Abisko Scientific Research Station.

Table 1. Plant species distribution in each of the chambers (Ch.1–8) at the three sites (Palsa, *Sphagnum* and *Eriophorum*)[a]. Other variables indicate the range of plant productivity as measured NEE (gC m^{-2}) based on all plants within a chamber, thaw depth (cm) and water table position relative to ground level (cm) that was recorded during the study period

	Dry palsa site			Wet *Sphagnum* site			Wet *Eriophorum* site	
Plant spp.	Ch.1	Ch.3	Ch.5	Ch.2	Ch.4	Ch.6	Ch.7	Ch.8
Eriophorum vaginatum	X	X	X	X	X	X		
Eriophorum angustifolium							X	X
Carex rotundata				X	X	X		
Rubus chamaemorus	X	X	X		X			
Betula nana			X					
Vaccinium uliginosum	X		X					
Empetrum hermaphroditum	X	X	X					
Andromeda polifolia	X	X	X	X	X	X		
Sphagnum fuscum	X							
Sphagnum spp.				X	X	X		
Polytrichum spp.	X	X	X					
Dicranum elongatum	X	X	X					
Lichens	X	X	X					
Others variables								
NEE (130 d)[b]	20–100 gC m^{-2}			60–150 gC m^{-2}			250–370 gC m^{-2}	
Thaw depth by August 30[b]	50 cm–55 cm			60cm – >100 cm			>100 cm	
Water table (wt) relative to ground surface[b]	–			(−)25 cm –(−)5 cm			(−)5 cm–5 cm	
Average wt position 2003/2004/2005[c]	–			−19 cm/−10 cm/−7 cm			−3 cm/−2 cm/−1 cm	

[a] A. Ekberg (personal communication, 2005).

[b] Range based on data from 2003 to –2005.

[c] Based on measurements during period of flux sampling (Fig. 5).

6.2 (36%) and 2.0 (12%) ha,respectively, with the remaining area consisting of open water and bare rock (Johansson et al., 2006).

Eight transparent automated chambers were used to quantify the surface exchange of trace gases at three sites representing the three subhabitats. Dominant plant species found in each chamber are noted in Table 1 as well as information about productivity, water table and thaw depth distribution at each site. In this study, we have focused on the growing seasons (approximately the period from period June 15 to August 30) of 3 yr (2003–2005).

2.2. Sampling and analyses

Total hydrocarbon (THC) exchange was measured semi-continuously with the automated chambers. The chamber system design also allowed manual sampling of chamber headspace CH_4 exchange. This enabled quantification of total NMVOC emissions when the CH_4 flux component was subtracted from the THC flux but not characterization of specific NMVOC species. The net exchange of CO_2 was also recorded with the automatic chambers and, in addition to this, dark chamber measurements were conducted to quantify total CO_2 respiration and thereby estimate gross primary production.

2.2.1. Automatic chamber system for measuring THC and CO_2 exchange. The automatic chamber system at the Stordalen Mire is similar to the system described in detail by Goulden and Crill (1997) (Fig. 2). Eight chambers were constructed of transparent Lexan® with aluminum frames. They were inserted into the ground to a depth of 5–10 cm in March 2001 and have stayed in place during the entire measurement period. They cover an area of 0.14 m^2 (38 cm × 38 cm) and chamber height varies from 25 to 45 cm depending on the vegetation and depth of insertion. A lid is closed and opened automatically with a double acting pneumatic piston (Bimba Manufacturing Company, IL, USA) connected to a compressor (GAST Manufacturing Inc., MI, USA) by 1/8″ nylon tubes. The pistons are actuated by air piloted four-way slider solenoid valves (Clippard Co., OH, USA) which makes it possible for the compressor pressure to keep the chamber lids open in all wind conditions. The closure interval was 5 min for each chamber every 3 h, that is, each chamber was closed for 3% of every day. Chamber closure intervals were kept as short as possible in order to minimize plant chamber effects and heating of the enclosed headspace.

The chambers were connected to the associated analysis system in a nearby, heated shack by 3/8″ polypropylene tubing, through which air samples were circulated at a rate of 4 l min^{-1}.

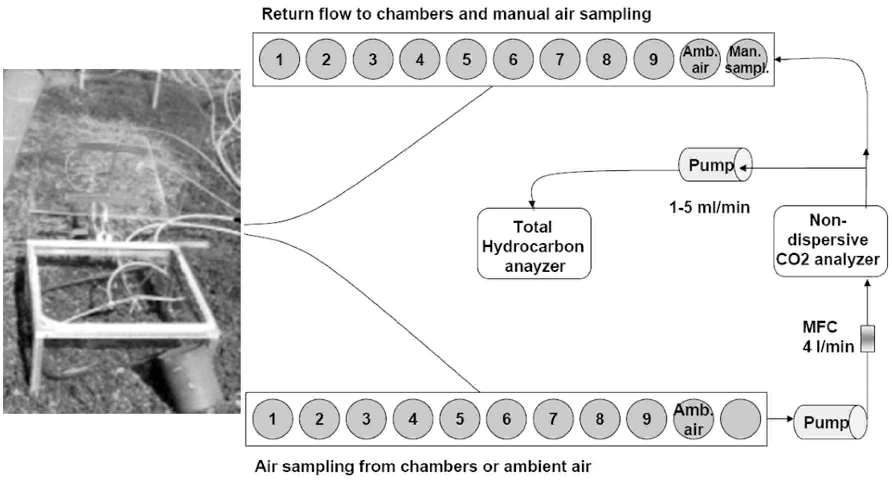

Fig. 2. Analytical system for the automated chambers. The numbers 1–9 indicate inlet and outlet for each chamber through which air was sampled to circulate by the analytical system (the non-dispersive CO_2 analyser and the total hydrocarbon analyser). The ports for ambient air analysis as well as the port for manual gas sampling downstream from the analytical instruments is also specified.

Three different tube lengths were used due to each site's distance from the control hut: 11 m (Palsa sites), 17 m (*Sphagnum* sites) and 23 m (*Eriophorum* sites). First, the sample air passed through a non-dispersive CO_2 analyser (Li820 and Li6262 CO_2/H_2O gas analyser, Li-Cor Biosciences, Lincoln, NE, used 2003–2004 and Vaisala GMP343 flow through CO_2 analyser, Vaisala, Helsinki, Finland used 2005). A small 24 vdc diaphragm pump was used to draw 1–5 ml min^{-1} from the main sample flow to the THC analyser (Model-300FID, California Analytical Instrument Inc., California, USA) and the remaining air was directed back to the chambers. Sample flow to the THC analyser was controlled with an electronic mass flow controller. Although the amount of gas pumped to the THC analyser was not compensated, we consider it not to be significant (for 5 min closure time, $<0.11\%$ of the total chamber volume). The raw signals from the analytical system to the datalogger (CR10X Campbell Scientific Inc., Utah, USA) were acquired with a frequency of 1/3 Hz and averaged every 15 s. Subsequently, data were transferred to a computer every 1 hr.

The spans of the analytical instruments were found to be very stable so calibration of the gas analytical instruments was conducted approximately every third week throughout the field seasons. Because the response of the THC analyser is proportional to the amount of carbon atoms in the sample (Christian and O'Reilly, 1986), calibration was conducted with span gases of 2 and 5 ppmv CH_4. Substitution by halogens, amines, hydroxyl groups or any electron capturing species may diminish the response of the THC analyser to some extent (Christian and O'Reilly, 1986), which means that the measurements are conservative if such compounds were abundant in the analysed sample air. The stability of the CO_2 analytical instruments were checked every 3 h by room air drawn through soda lime as an approximate CO_2 zero. For calibration of CO_2 analytical instruments, CO_2-free UHP air and 350 ppmv CO_2 span gas were used.

THC flux was calculated based on a linear regression of change in the headspace mixing ratio with time. The period of chamber closure on which flux calculations are based, is 3 min starting 30 s after the lid closes (i.e. 13 readings of THC mixing ratios with 15 s interval).

Net uptake of CO_2 was calculated using the 2.5-min period after chamber closure that has the steepest slope of change in the headspace mixing ratio with time. When there was an efflux of CO_2 to the atmosphere, the flux was determined from the 2.5-min period of chamber closure that has the highest r^2 of the corresponding slope, that is, the most linear portion of the curve. Eight sequential 2.5 min fluxes were calculated using subsequent 15s average values as the first point. In choosing the best of these eight calculations, the highest r^2 value determines CO_2 efflux and the steepest decreasing slope determines the CO_2 uptake. Usually, the first flux calculation was used, but occasionally a subsequent set yields a stronger r^2 or slope. The reason for treating CO_2 uptake differently from release is that plants saturate very quickly at high light and by choosing the steepest slope, we were assuring that the most accurate CO_2 uptake rates were chosen. At night, photosynthesis is not occurring so the highest r^2 ensures that flux represents the increase in CO_2 concentration over time that is closest to linear. Logarithmic algorithms were specifically not used because of the high sensitivity of initial slope to outliers.

2.2.2. Measurements of methane (CH_4) exchange. Manual samples of chamber headspace air were taken from the main sample air-flow downstream from the gas analysers. A manually actuated solenoid opened a port in the return gas manifold from which aliquots were taken with 10 ml BD plastic syringes. An ambient air reference sample was taken 1 min before chamber closure. Then, four samples were taken 1 min apart starting 30 s after chamber closure, which corresponds to the same 3 min period used for THC flux calculation described above. CH_4

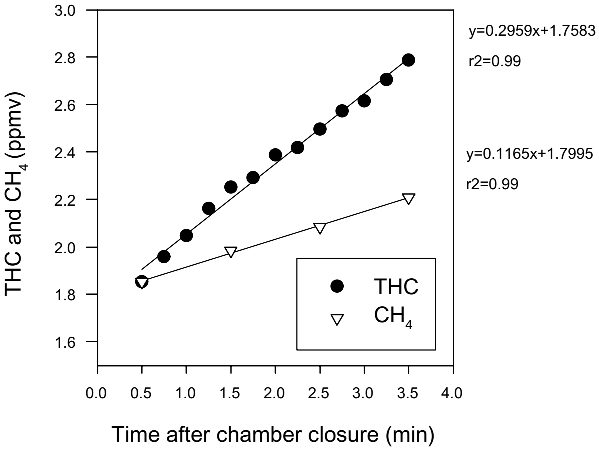

Fig. 3. Example of concentration change over time in one of the chambers on July 5, 2004. Based on the slope of the mixing ratio over time, the flux is calculated for each trace gas component. The subtraction of CH_4 from THC resulted in an estimation of NMVOC flux.

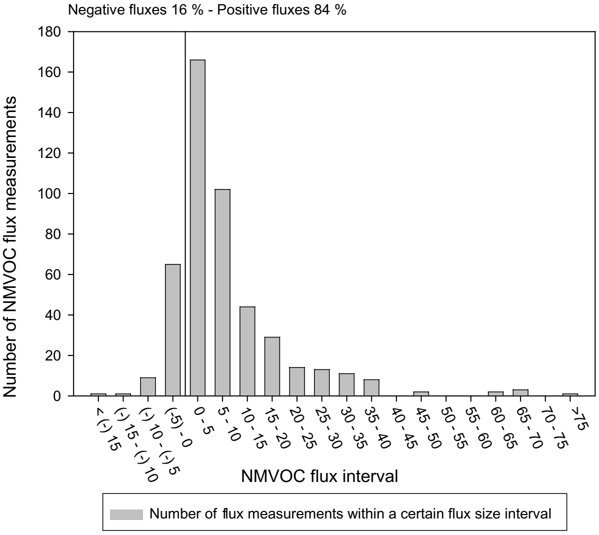

Fig. 4. Histogram of the frequency distribution of NMVOC fluxes. The data distribution is skewed towards lower values with a grand mean of 8.0 ± 0.54 mgC m^{-2} d^{-1} (mean ± 1 *SE*; $n = 470$). 84% of the observations were positive fluxes (i.e. emission to the atmosphere).

flux was calculated from the linear regression of change in the headspace mixing ratio with time. CH_4 analyses were carried out on a Shimadzu GC FID at the Abisko Scientific Research Station within 10 h after sampling using a 2 m × 3.2 mm stainless steel column packed with Porapak N at 40 °C. Ultra high purity He or N_2 was used as carrier gas at 25 ml min^{-1}. Samples were compared to a 1.96 ppmv standard gas mixture (AGA, Sweden). The average precision of analysis, based on 16 repeated injections of standard (8 before and 8 after sample analysis) for every daily analysis run, was 0.01 ± 0.01 ppmv ($n = 58$ d; mean ± 1 *SD*) and 0.53 ± 0.58% ($n = 58$ d, mean ± 1 *SD*). The minimal detectable CH_4 flux using only the analytical uncertainty (average flux ±1 *SD* different from zero) over 3 min was 1.8 mg CH_4 m^{-2} d^{-1}. Manual samples were collected approximately three times a week during the specified growing seasons. All CH_4 samples were collected during daytime between 9 a.m. and 3 p.m. except for 1 d in July 2004 [day of year (DOY) 198] when a 24 h sample cycle was conducted.

2.2.3. Calculation of non-methane volatile organic compound (NMVOC) exchange. The manually determined CH_4 flux component was subtracted from the THC exchange to calculate the NMVOC fluxes (Fig. 3). Before making this calculation, THC and CH_4 flux raw data were examined carefully. At high emissions sites (*Sphagnum* and *Eriophorum* sites) fluxes always showed consistent increase over time. Therefore, data selection could be based on statistically significant regressions with time and only significant fluxes were included in the analysis (CH_4 flux $n = 4$; THC flux $n = 13$; $p < 0.05$). At the low emission site (Palsa site), this filtering criteria could not be used because fluxes near or below the minimal detectable flux will always give a low r^2 and are likely to be statistically non-significant. Fluxes that were more negative than -10 mgC m^{-2} d^{-1} at the low emission site were examined and only included if there was a consistent decrease over time supported by all measurement points and if the initial value was close to ambient. CH_4 fluxes occasionally exceeded THC fluxes, most frequently in the Palsa site. This resulted in negative NMVOC estimates (Fig. 4). For high emission sites negative NMVOC fluxes were probably unrealistic. However, we accepted CH_4 fluxes exceeding THC fluxes with up to 25% to ensure the average NMVOC flux calculations were conservative and not overestimates. An additional data selection criterion was that the calculated initial value after chamber closure had to be close to the ambient reference sampled 1 min before chamber closure. Using these criteria, 470 estimates remained after data evaluation (the total number of observations rejected was 46).

2.2.4. Data analysis. A two-way ANOVA with years, sites and chambers as factors was used to determine the variance of flux dynamics between chambers within a specific site as well as between sites and years. DOY was used as a covariate to account for potential linear relationships between NMVOC flux and the DOY. The ANOVA was performed with log transformed values because data were not normally distributed, that is $[\log_{10}(Y + 100)]$. The constant +100 was used to avoid negative values.

2.2.5. Environmental parameters. Photosynthetic active radiation (PAR) and temperature were continuously logged by the automatic system previously described. Water table position relative to ground level was measured manually three to five times per week at all sites. Air pressure and precipitation were recorded at Abisko Scientific Research Station.

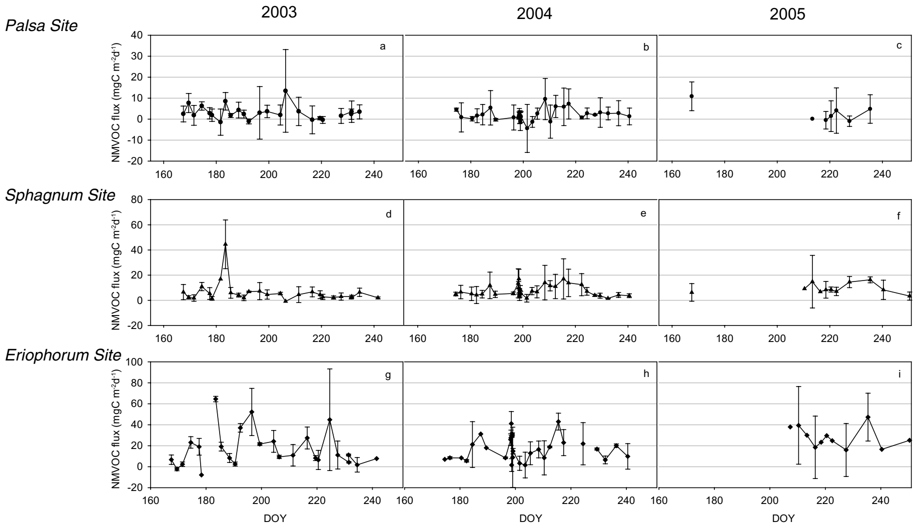

Fig. 5. Seasonal pattern of NMVOC emissions at three sites (Palsa, *Sphagnum* and *Eriophorum*) during 3 yr (2003–2005). The points are set averages with error bars representing the standard deviation of the mean ($n = 1$–3).

3. Results

NMVOC fluxes (THC flux–CH_4 flux) ranged from -17.5 to 79.1 mgC m^{-2} d^{-1} and were generally positive (Fig. 4). The grand mean of all flux measurements with no area weighting is 8.0 ± 0.54 mgC m^{-2} d^{-1} (mean ± 1 *SE*; $n = 470$) and the median is 4.7 mgC m^{-2} d^{-1}. Over the 3 yr (2003–2005), the set averaged fluxes (average of all the chambers in a site during each 3 h measurement cycle) at the Palsa site varied between -4.4 and 13.4 mgC m^{-2} d^{-1} (Fig. 5a–c) and the set average flux at the *Sphagnum* site ranged between -0.8 and 44.4 mgC m^{-2} d^{-1} (Fig. 5d–f). Corresponding minimum and maximum set average fluxes at the *Eriophorum* site were -7.9 and 64.5 mgC m^{-2} d^{-1} (Fig. 5g–i). Significant differences between individual chambers within each site could not be detected with a two-way ANOVA ($p = 0.481$) of log-transformed values.

There was no significant linear relationship ($p = 0.617$) between NMVOC flux and the DOY (Fig. 5a–i). In some years at the *Sphagnum* site (2004) and the *Eriophorum* site (2003–2004), higher fluxes may have occurred during the mid growing season (Fig. 5a–i). In 2005, the data set only covers the end of the summer (August) so we cannot make interpretation about the seasonal pattern. The early season data in 2005 were rejected due to maintenance problem with the THC gas analytical instrument.

The two-way ANOVA of the log-transformed data did reveal significant differences between the sites ($p < 0.0001$). The NMVOC flux followed the moisture gradient and increased from the Palsa site to the *Sphagnum* site with the *Eriophorum* site having the highest fluxes and this trend is consistent in individual years (Fig. 5a–i). The averaged fluxes for each subhabitat, based on all measurements from the 3 yr, were 2.25 ± 0.41, 6.68 ± 0.46 and 18.56 ± 1.59 mgC m^{-2} d^{-1} (mean ± 1 *SE*; $n = 178$, 175 and 117), respectively for the Palsa, *Sphagnum* and *Eriophorum* sites (Table 2). The two wetter sites are thereby the most significant NMVOC emitting sites found on the mire while sites on cold drained peat are comparatively low emitters.

In order to account for the fact that 2005 only included NMVOC flux measurements made during August, a comparative study of fluxes measured during this specific period of the growing season was also conducted (Fig. 6). The two-way ANOVA of the log-transformed data did still reveal significant differences ($p < 0.0001$) between the sites. Averaged August fluxes, based on data from all 3 yr of study, were 1.56, 6.74 and 19.35 mgC m^{-2} d^{-1} for the Palsa, *Sphagnum* and *Eriophorum* site, respectively (Fig. 6a). These flux numbers are in the same order of magnitude as the ones described above where no consideration was taken to the fact that the different years covered slightly different periods. There were significant differences in the August fluxes between the years ($p = 0.014$) at the wet sites. The *Sphagnum* site was characterized by a consistent increase in the August fluxes throughout the study period (3.57 in 2003; 7.81 in 2004; 9.77 in 2005, mgC m^{-2} d^{-1}; Fig. 6b). The *Eriophorum* chambers show the same pattern as the *Sphagnum* site with increased emissions in August over the years (13.98 in 2003; 20.12 in 2004; 26.04 in 2005, mgC m^{-2} d^{-1}; Fig. 6b). On the other hand, interannual variability at the dry Palsa site was characterized by highest August fluxes in 2004 (0.80 in 2003; 3.19 in 2004; 0.16 in 2005, mgC m^{-2} d^{-1}; Fig. 6b).

A significant relationship was found between increased negative values of net ecosystem exchange (NEE) of CO_2 and NMVOC emissions. When individual point measurements of NEE were correlated with individual NMVOC fluxes for all sites and years combined, the relationship was found to be significant but the data were widely distributed ($y = -2.5996x + 3.2291$; $r^2 = 0.16$; $p < 0.05$). To focus on the photosynthetic component of NEE, an analysis was made between NMVOC fluxes and NEE

Table 2. Comparison of NMVOC flux estimates to other studies

Vegetation types	Site	Average NMVOC flux[a]	Max NMVOC flux[b]	Reference
Palsa vegetation	Stordalen Mire	2.25	36.15	This study
	Stormossen[c]	0.61	1.99	Janson and De Serves (1998)
Sphagnum spp.	Stordalen Mire	6.68	22.54	This study
	Hudson Bay Lowland[d]	9.33	No data	Klinger et al. (1994)
	Ryggmossen[e]	6.241	17.28	Janson et al. (1999)
	Siikaneva[f]	0.86	16	Haapanala et al. (2006)
	Stormossen/Salmisuo[g]	14.27	43.3	Janson and De Serves (1998)
	Siikaneva[h]	No data	2.2	Hellén et al. (2006)
Eriophorum spp.	Stordalen	18.56	79.05	This study

Note: All fluxes presented as mgC m^{-2} d^{-1}.

[a] Average NMVOC flux is estimated from data sampled during the growing season. See specific study for details on VOC species, sampling period and sampling technique.

[b] Maximum flux measured in each study.

[c] Boreal palsa site, Sweden. VOCs: isoprene, ethene and propene. Period: June 5–August 19. Technique: chamber.

[d] *Sphagnum* bog, Canada. VOCs: isoprene and monoterpene. Sampling period: May–October. Emission potential = average for several vegetation types. Technique: chamber.

[e] Boreal *Sphagnum* fen, Sweden. VOCs: isoprene and monoterpene. Period: June (1 d) August (1 d). Technique: chamber. Note: maximum flux is isoprene.

[f] Boreal *Sphagnum* fen, Finland. VOCs: Isoprene. Period: May–September. Technique: REA. Note: Averaged flux from modelled data and maximum is an estimate from data point in figure.

[g] Boreal *Sphagnum* fen, Sweden/Finland, VOCs: isoprene, ethene and propene. Period: June 5–August 19. Technique: chamber.

[h] Boreal *Sphagnum* fen, Finland. VOCs: isoprene. Period: Emission potential June–October (2004), Maximum flux August 19 (2005). Technique: chamber.

at high PAR (>1000 μmol $s^{-1}m^{-2}$) which shows a stronger relationship ($r^2 = 0.22$; $p < 0.05$; Fig. 7). When seasonal chamber averages of the trace gas components were used in the analysis, the relationship between NMVOC fluxes and NEE became even more clear ($r^2 = 0.63$; $p < 0.05$; Fig. 8). These findings illustrates an overall seasonal connection between NMVOC emissions and NEE (Fig. 8) and that short-term (hourly) NMVOC emissions are most strongly related to the photosynthetic component of NEE (seasonal chamber averages of NEE were based on data from the same days as NMVOC measurements were conducted).

There was a tendency toward increased NMVOC emissions with higher temperatures and even though the scatter was large, the relationships were found to be significant combining all sites and years ($y = 0.2020x + 4.1424$; $r^2 = 0.02$; $p = 0.0076$). Individual NMVOC fluxes from all sites and years were also significantly correlated with PAR, however, the pattern of widely scattered data was again present resulting in poor predictive power ($y = 0.0030x + 3.5065$; $r^2 = 0.0104$; $p = 0.0495$). NMVOC emissions appeared to be independent of air pressure, precipitation and primary production when direct linear relationships were tested.

4. Discussion

The results indicate substantial emissions of NMVOCs from the studied peatland. The flux rates from our subarctic site were of the same order of magnitude as fluxes in previously studied boreal environments (Table 2). Fluxes from our Palsa site were somewhat higher than fluxes measured at boreal hummock sites by Janson and DeServes (1998) at Stormossen in Sweden. The mesic *Sphagnum* spp. site fluxes from Stordalen agree very well in magnitude and range with other studies (Klinger et al., 1994; Janson et al., 1999). We could not find NMVOC flux measurements from other sites similar to the wet *Eriophorum* spp. site.

Some of the differences in the magnitudes of the fluxes may be partly explained by differences in methodology. In this study, total NMVOC fluxes were measured without distinguishing different chemical species, while previous studies typically measured a few selected NMVOC species. To our knowledge, this study also includes more flux measurements over a longer period (three growing seasons) than previous studies in similar regions. The major drawback with our method is that fluxes are calculated as the difference between THC and CH_4 fluxes measured separately (see Section 2), and this procedure may introduce errors but on the other hand should be more representative for the total NMVOC flux. Of course, identification of specific NMVOCs emitted from the studied areas is also of interest and other groups working in Stordalen Mire are pursuing these analyses.

Negative fluxes implying deposition were sometimes observed and most of the negative fluxes (74%) were measured at the low emission dry Palsa site. At this site, negative fluxes

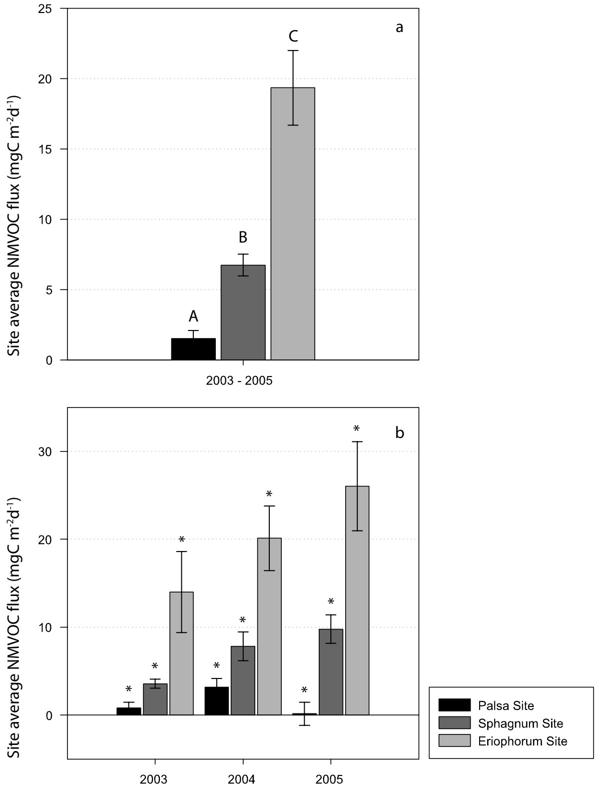

Fig. 6. Site averages of NMVOC flux for each vegetation type, based on August data. (a) Site averages all years included. (b) Site averages per year. Error bars represent standard error of the mean (Palsa site 2003 $n = 27$, 2004 $n = 23$, 2005 $n = 16$; *Sphagnum* site 2003 $n = 27$, 2004 $n = 22$, 2005 $n = 22$; *Eriophorum* site 2003 $n = 17$, 2004 $n = 14$, 2005 $n = 12$). Result from ANOVA is indicated by letters or asterisks above each site. By having no letters in common, it shows that the emissions at each site are significantly different from each other, at $p < 0.005$ (a). Asterisks indicate sites where emissions are significantly different between years, at $p < 0.005$ (i.e. all sites; b).

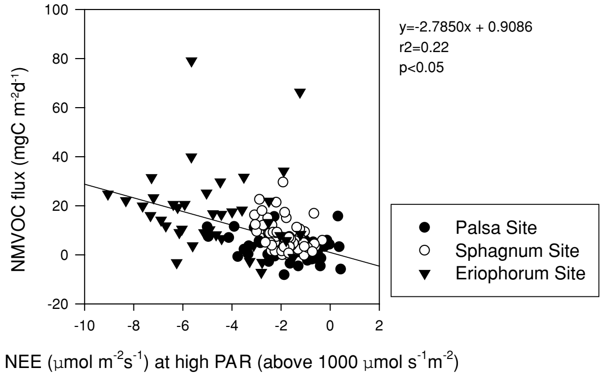

Fig. 7. NMVOC emissions versus NEE of CO_2 by the vegetation at high PAR (>1000 μmol $s^{-1}m^{-2}$). NEE is negative when there is a net uptake of CO_2 to the biosphere from the atmosphere as opposed to NMVOC which is mostly positive and accounts for a net emission to the atmosphere.

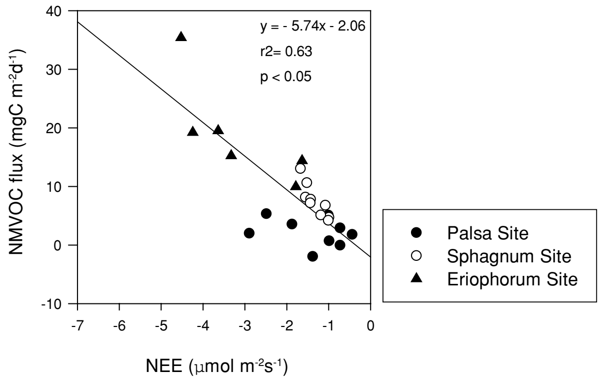

Fig. 8. NMVOC emissions versus NEE of CO_2 by the vegetation considering seasonal averages for individual chambers at all sites. NEE is negative since it accounts for a net uptake of CO_2 to the biosphere as opposed to NMVOC which is mostly positive and accounts for a net emission to the atmosphere. The averages of seasonal CO_2 net ecosystem exchange are based on CO_2 flux measurements from the same days as NMVOC measurements were conducted.

possibly could be related to methodological difficulties in calculating the NMVOC flux from low THC and CH_4 fluxes that are close to their limit of detection as discussed above. However, these fluxes could also represent a real atmospheric loss of NMVOCs. Altogether at the three sites during the 3 yr, 84% of the flux calculations were positive (Fig. 4). Hence, in spite of a few negative flux measurements, subarctic mires are likely to represent net sources of NMVOCs to the atmosphere.

In general, previous studies indicate that isoprene emissions increase through the spring, peak in mid-summer and decline during the autumn (Harley et al., 1999). This seasonal pattern is also described for NMVOCs other than isoprene (Kesselmeier and Staudt, 1999; Penuelas and Llusia, 2001). However, there are very few data on seasonal patterns of NMVOC emissions at northern latitude sites. At a *Sphagnum* spp. fen in Finland, the Siikaneva fen, a seasonal pattern over the period April to October was found, with higher fluxes in the mid summer (Haapanala et al., 2006). A hummock site at Stormossen, Sweden, showed a linear increase of emission throughout the season, but the fluxes were low and only 4 d of sampling (3 fluxes per day) were included in the study (Janson and De Serves, 1998). *Sphagnum* spp. sites (Stormossen, Sweden and Salmisuo, Finland) in the same study (Janson and De Serves, 1998) did not show a clear seasonal pattern of either linear increase or bell shaped emission patterns. Similarly, there was no obvious seasonal pattern revealed from the data of standard emission potentials studied at the Siikaneva fen (Hellén et al., 2006). Highest fluxes were recorded in August but the authors conclude that more measurements are needed to verify conclusions about seasonal patterns. High fluxes of isoprene and monoterpene were also recorded in August at Ryggmossen, but only 2 d of sampling were conducted from which you cannot make any conclusions about seasonal patterns (Janson et al., 1999). A study across a successional gradient of ecosystem development in the Hudson Bay lowlands only reported average flux values for the ecosystem type similar to the *Sphagnum* site at Stordalen Mire (i.e. *Sphagnum* bog), and did not give any information about seasonal emission dynamics (Klinger et al., 1994). At Stordalen, the results of this study showed that there was not a simple linear increase in NMVOC emission over time at any of the sites during the 3 yr. However, there may have been a seasonal pattern at the *Sphagnum* site (2004) and the *Eriophorum* site (2003–2004) with highest emissions in the middle of the growth season, but this pattern was not very pronounced and variability between days or weeks were usually greater than variability over the season. The Palsa site does not show a seasonal pattern, instead there are consistently low fluxes throughout the growing seasons (2003–2004). Data are too scarce to allow any interpretations about the seasonal pattern for 2005.

The amount of NMVOCs emitted differed between studied subhabitats and vegetation types, increasing from Palsa site via the *Sphagnum* site to the *Eriophorum* site (Figs. 5 and 6). This is most likely driven by the fact that plant species vary in their potential to produce and emit NMVOCs. Further, higher NMVOC emissions were found to be significantly related to an increase in the rate of CO_2 net uptake by the vegetation and this may also explain the differences in flux regimes at the three subhabitats. There was a clear linear relationship between seasonal chamber averages of NEE and NMVOC emissions when all sites were included in the analysis (Fig. 8). Because this correlation was weaker with more dispersed data when individual measurements of NMVOC emissions and NEE were considered (Fig. 7), NEE apparently does not directly control NMVOC emissions although seasonal averages of NEE may be used to estimate the relative size of NMVOC emissions. Furthermore, NMVOC emissions appears to be most strongly related to the photosynthetic component of the CO_2 metabolism because NMVOC fluxes were better correlated with NEE at high PAR (above 1000 μmol $s^{-1}m^{-2}$) than with NEE at all PAR levels. It should be noted that NEE of CO_2 includes autotrophic processes such as plant metabolism as well as heterotrophic processes related to degradation of organic matter (e.g. soil respiration). Other studies suggests that NMVOC production and emissions are closely related to plant metabolism (e.g. Kesselmeier and Staudt, 1999), however in this study we cannot distinguish to what extent production of NMVOCs was linked to plant metabolism or organic matter degradation processes in the soil.

An environmental variable that differed between the sites studied at the Stordalen Mire is the water table (Table 1). In this study, we believe that soil moisture, or water level, may indirectly be linked to the NMVOC emissions at each site by affecting the plant species distribution, productivity or soil organic matter decomposition. Due to low water table variability at the *Eriophorum* site and the absence of measurable water table at the dry Palsa site, seasonal variability in water table position within a site is primarily relevant for the *Sphagnum* site where the seasonal variability in water table position for example can be due to precipitation and/or active layer depth. At similar study sites in boreal Sweden and Finland, the moisture content of *Sphagnum* spp. has been discussed as being a controlling factor of NMVOC release, where higher moisture content implied higher emissions (Janson and De Serves, 1998). At the *Sphagnum* site at Stordalen, there is a correlation between seasonal NMVOC fluxes and seasonal water table position at the *Sphagnum* site, where years with wetter conditions shows higher NMVOC emissions. However, we do not know if the water table position affects fluxes in itself or indirectly by affecting, for example, NEE.

There was a significant difference in NMVOC emissions between years at wet sites when August fluxes are compared. However, even though statistically significant, this difference appears smaller than differences between sites (Fig. 6a and b). We did not find any evident explanations for either the interannual variability or the potential seasonal pattern but possibly factors influencing plant communities and net uptake of CO_2 (e.g. temperature, light and moisture) can affect not only spatial but also temporal patterns of the fluxes. The analysis of temperature and light dependency on NMVOC emissions in this study showed significant positive relationships but with widely scattered data. Previous studies conclude that short-term (hours to days) NMVOC emission capacity may depend on weather conditions (PAR and temperature) of the previous days as concluded from a study above an oak tree forest (Harley et al., 1999; Sharkey et al., 1999) and from frequent observations of isoprene emissions correlation with PAR and temperature (e.g. Kesselmeier and Staudt, 1999; Penuelas and Llusia, 2001). However, there are obvious problems identifying such short term controls on NMVOCs in a study like this where we did not measure specific VOC species' response to different environmental variables. Controlled laboratory studies and small enclosure measurements are needed to quantify the light and temperature dependencies of specific VOC emissions, and such studies are currently under progress by other groups working on the Stordalen mire. This study indicates that temporal variability in NMVOC fluxes seems less predictable than differences between specific subhabitats, particularly at a short-term basis (within seasons).

Considerable amounts of NMVOCs are being emitted from three typical subarctic environments. These environments are highly sensitive to climate change (ACIA, 2005). As shown in earlier studies, the Stordalen mire has undergone substantial changes in plant species distribution since the 1970s, (Malmer et al., 2005; Johansson et al., 2006). One of the main causes of these changes is thought to be warmer temperatures shifting the amount and distribution of permafrost, which has altered the surface topography and hydrology of the peatland and thereby affected plant species distribution. The loss of higher dry Palsa-like habitats will dramatically increase NMVOC fluxes. The Stordalen *Sphagnum* site is considered an intermediate melt feature and, as the permafrost thaws completely, the hydrology will change and the site will become dominated by *Eriophorum*

Table 3. Flux measurements (site averages) of NMVOCs (mgC m^{-2} d^{-1}) and estimates of total NMVOC emissions per growing season (kgC gs^{-1}) are presented and a comparative study of the 1970 and 2000 NMVOC budgets is available. Average NMVOC flux for all subhabitats on the mire is area-weighted average. Vegetation type area distribution at Stordalen (ha) and comparative fluxes of CO_2 and CH_4 are also presented (Johansson et al., 2006)

	Area			Total flux (kgC gs^{-1})[b]	
Vegetation type	1970	2000	Areal fluxes (mgC m^{-2} d^{-1})	1970	2000
			NMVOC-C		
Palsa	9.20	8.30	2.25 ± 0.41[d]	32	29
Sphagnum spp.[a]	6.00	6.20	6.68 ± 0.46[d]	61	63
Eriophorum spp.	1.30	2.00	18.56 ± 1.59[d]	37	57
All subhabitats	16.50	16.50	5.89	130	149
			CO_2-C		
Whole mire[c]			−180	−4075	−4699
			CH_4-C		
Whole mire[c]			50	1124	1373

Notes: Daily and gs averages for CO_2-C and CH_4-C are from 2000 data and daily and gs averages for NMVOC-C are from 2003 to 2005 data.

[a] *Sphagum* site area in this study accounts for two vegetation classes (Semiwet and Wet) described in Johansson et al. (2006).

[b] Growing season (gs) in this table represent May–October (153 d).

[c] Whole mire fluxes from Johansson et al. (2006) includes open water area flux (0.08 CO_2-C, 0.004 CH_4-C; mgC m^{-2} d^{-1}).

[d] Mean ± 1 *SE*; Palsa site $n = 178$, *Sphagnum* site $n = 175$, *Eriophorum* site $n = 117$.

sp. Such changes in hydrology and plant community structure would be accompanied by a threefold and a ninefold increase in the NMVOC emissions.

Keeping in mind the difficulties in up-scaling local flux studies, we extrapolated our results to try to better understand the environmental change observed at Stordalen and its effect on the carbon exchange (Table 3). For 1970, our estimate of total area weighted accumulated emissions during the May–October period would be 130 kgC. For 2000, the equivalent emission was 150 kgC, indicating a 15% increase in emission to the atmosphere over 30 yr during the summer season (Table 3). On a regional basis, a substantial increase in VOC emissions could affect the tropospheric sink term for CH_4 and feedback into the local climate.

In Table 3, we also show NMVOC emissions compared to the net carbon exchange of CO_2 and CH_4 at Stordalen (Johansson et al., 2006). The amount of carbon emitted as NMVOCs during the growing seasons (2003–2005) accounts for approximately 10% of the total hydrocarbon emissions (1522 kgC; CH_4-C and NMVOC-C). The total net exchange of carbon (net uptake of CO_2-C and net efflux of THC considered) is estimated to −3177 kgC of which NMVOC-C accounts for 5%. There are similar ratios during the two periods 1970 and 2000. The significant amount of NMVOC-C, compared to the total net exchange of carbon, illustrates the importance of including NMVOCs in the trace gas research of these environments.

Boreal and subarctic peatlands cover approximately 3.5 million km^2 (Gorham, 1991) in the northern hemisphere. When applying the area weighted average flux value of 5.89 mgC m^{-2} d^{-1} (Table 3) from Stordalen to this larger region of peatlands, we calculate that the total annual emission of NMVOCs could be 3.1 Tg C yr^{-1} (from May to September). The total annual global natural NMVOC flux is estimated to range between 1150 and 1500 TgC (Guenther et al., 1995; Penuelas and Llusia, 2001). This implies that NMVOCs from boreal and subarctic peatlands constitute about 0.3% of the total natural emissions based on our estimations (using Guenther et al., 1995 as reference for total global natural emissions). For comparison, tropical (seasonal and rain) forests, which are the highest NMVOC emitting vegetation, are estimated to have emissions of ∼265 Tg C yr^{-1}. This number represents approximately 23% of the global total emissions (Guenther et al., 1995).

5. Conclusions

NMVOC emission rates varied at the three subhabitats with highest emissions from the *Eriophorum* and *Sphagnum* sites. The emission dynamics seem to be related to plants species distribution and long-term variation in NEE of CO_2, but considerable short-term variation of the fluxes makes the temporal variability less predictable and relations to temperature and/or PAR were weak.

Our results indicate that even though boreal and subarctic peatlands are minor sources of NMVOCs globally (0.3%), the rate of emissions still represent a substantial carbon flux in a subarctic peatland environment. Total NMVOC emission from the Stordalen mire (17 ha) was estimated to consist of ∼150 kgC during a growing season with 150 d. This accounts for ∼5% of the total net carbon exchange (−3177 kgC) at the mire during the same period, net uptake of CO_2 and net emission of total volatile hydrocarbons considered. The emissions are likely to increase due to potential vegetation changes as a result of global warming.

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