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**Sub-arctic BVOC
ecosystem flux**

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BVOC ecosystem flux measurements at a high latitude wetland site

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Abstract

In this study, we present summertime concentrations and fluxes of biogenic volatile organic compounds (BVOCs) measured at a sub-arctic wetland in northern Sweden using a disjunct eddy-covariance (DEC) technique based on a proton transfer reaction mass spectrometer (PTR-MS). The vegetation at the site was dominated by *Sphagnum*, *Carex* and *Eriophorum* spp. The performance of the DEC system was assessed by comparing H_3O^+ -ion cluster formed with water molecules ($\text{H}_3\text{O}^+(\text{H}_2\text{O})$ at m37) with water vapour concentration measurements made using an adjacent humidity sensor, and from a comparison of sensible heat fluxes for high frequency and DEC data obtained from the sonic anemometer. These analyses showed no significant PTR-MS sensor drift over a period of several weeks and only a small flux-loss due to high-frequency spectrum omissions. This loss was within the range expected from other studies and the theoretical considerations.

Standardised (20°C and $1000\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$ PAR) summer isoprene emission rates of $323\ \mu\text{g C m}^{-2}$ (ground area) h^{-1} were comparable with findings from more southern boreal forests, and fen-like ecosystems. On a diel scale, measured fluxes indicated a stronger temperature dependence when compared with emissions from temperate or (sub)tropical ecosystems. For the first time, to our knowledge, we report ecosystem methanol fluxes from a sub-arctic ecosystem. Maximum daytime emission fluxes were around $270\ \mu\text{g m}^{-2}\ \text{h}^{-1}$ (ca. $100\ \mu\text{g C m}^{-2}\ \text{h}^{-1}$) and measurements indicated some nocturnal deposition.

The measurements reported here covered a period of 50 days (1 August to 19 September 2006), approximately one half of the growing season at the site, and allowed to investigate the effect of vegetation senescence on daily BVOC fluxes and on their temperature and light responses. Long-term measurements of BVOC are still lacking for nearly all ecosystems and only a very few studies about seasonal or even interannual variation of BVOC emissions have been published so far, particularly for northern ecosystems. The results presented here will be useful for testing process

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understanding obtained in laboratory studies and for model evaluation, improving our understanding of biogeochemical cycles in a region which is likely to be sensitive to climate change and currently undergoes rapid changes due to global warming.

1 Introduction

5 The global emission of biogenic volatile organic compounds (BVOC) from terrestrial vegetation is estimated to be ca. 1000 Tg C a^{-1} (e.g. Guenther et al., 1995; Lathière et al., 2006; Seco et al., 2007) with an associated strong impact on atmospheric chemistry. BVOC consume or produce tropospheric ozone, depending on atmospheric physicochemical conditions like the levels of NO_x , and influence the levels of OH and hence methane lifetime (Derwent et al., 1995; Atkinson, 2000; Poisson et al., 2000; Ortega et al., 2007). Furthermore, BVOCs are known to initiate and foster the production of secondary organic aerosols (SOA, Hoffmann et al., 1997; O'Dowd et al., 2002; Kulmala et al., 2004) that scatter and absorb radiation and act as cloud condensation nuclei. Despite their high importance for global chemistry and climate, many processes relating to the physiology and atmospheric reactions of BVOCs remain poorly understood. Large uncertainties are introduced not only by the poorly quantified source and sink distribution, but also by an incomplete understanding of ecological and physiological controls (Niinemets et al., 2004; Arneth et al., 2008a). Furthermore, it has been shown that some VOC can react very rapidly after emission to form a sink for oxidants which has not been previously accounted for (Di Carlo et al., 2004; Holzinger et al., 2005; Karl et al., 2008). These highly reactive VOCs might be a defence mechanism for plants against atmospheric oxidants and their oxidation products may act on a larger scale due to their relatively high stability and thus contribute effectively to SOA production (Holzinger et al., 2005).

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Leaf BVOC emissions have been measured from a wide range of vegetation types and species (e.g. Kesselmeier and Staudt, 1999; Seco et al., 2007), but the data are mostly restricted to relatively short-term campaigns using leaf or branch cuvette techniques. A number of studies have investigated the canopy-atmosphere exchange of BVOC using the gradient method, relaxed eddy accumulation (REA) methods, as well as disjunct eddy covariance techniques (DEC, Gallagher et al., 2000; Rinne et al., 2000; Rinne et al., 2001; Schade and Goldstein, 2001) and, in the case of isoprene, direct eddy covariance with fast response sensors (Rinne et al., 2002; Pressley et al., 2005). Recently, the development of the proton transfer mass spectrometer (Lindinger et al., 1998; de Gouw et al., 2003; de Gouw and Warneke, 2007), in conjunction with disjunct eddy covariance techniques has led to an increased availability of flux data from a wider range of ecosystems including tropical and mid-latitude forests, grassland and crops (e.g. Karl et al., 2001; Karl et al., 2002; Grabmer et al., 2004; Brunner et al., 2007; Custer and Schade, 2007) and covering continuously periods of days to weeks. These measurements have drawn attention to the large temporal and spatial variability in ecosystem emission rates. Even within similar vegetation classes, maximum emissions can vary by a factor of ten or more, depending on the species composition (Rinne et al., 2000; Karl et al., 2003; Pressley et al., 2005), while measurements that covered an entire growing season or longer point to a significant influence of changing atmospheric conditions, growth stages or decay of vegetation on the emission of VOCs from different ecosystems (Fuentes et al., 1999; Westberg et al., 2000; Karl et al., 2003; Pressley et al., 2005; Brunner et al., 2007). Canopy flux data from a wide range of vegetation types and climates are thus crucial to evaluate process descriptions and emission rates calculated with regional and global BVOC emission models. To do so BVOC flux measurements should ideally span not only short-term campaigns but also address at least seasonal, better interannual variability (Pressley et al., 2005). Furthermore, ecosystem carbon and water fluxes measured side-by-side with BVOC flux emissions (e.g. Gallagher et al., 2000; Simon et al., 2005) are valuable information

to illuminate flux controls on ecosystem scale and to quantify all gaseous carbon fluxes exchanged with the atmosphere.

One region for which virtually no information on BVOC emissions exist are the high northern latitudes – ecosystems that are likely to experience warming, permafrost melting and changes in vegetation distribution in the coming decades. Global emission models attribute only a small percentage of total BVOC emissions, mainly of isoprene and monoterpenes, to latitudes above ca. 50° N, due to the short summers with relatively cool temperatures, and due to vegetation with (particularly in case of isoprene) low emission potentials (Guenther et al., 1995; Arneth et al., 2008b). However, regionally these emissions are important as, for example, emissions from boreal forests have been shown to contribute to growth of aerosol particles and to affect total aerosol mass (Kulmala et al., 2000, 2004; Tunved et al., 2006).

With the exception of a very few studies (Rinne et al., 2000; Rinne et al., 2005; Haapanala et al., 2006), most work on BVOC emissions in boreal ecosystems has been done using chamber or microcosm techniques (Janson et al., 1999; Hellén et al., 2006; Tiiva et al., 2007a,b; Bäckstrand et al., 2008; Ekberg et al., 2008). Here, we present for the first time DEC-measurements of BVOC exchange between the atmosphere and a sub-arctic wetland. The measurements have been taken as part of a collaborative project on the full gaseous C-balance (CO₂, CH₄ and BVOC) on leaf, microcosm and ecosystem scale in a system that currently undergoes fast permafrost melting. Johansson et al. (2006) reported a significant decline of permafrost and a change of vegetation patterns from hummock vegetation to wet-growing vegetation at the experimental site used in this study during a 30-year period (1970 to 2000). Our objectives here are to present the general performance of the BVOC measurement system as well as a first analysis of BVOC data covering nearly one half of the short growing season.

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2 Methods

2.1 Experimental site

Measurements were made in a sub-arctic wetland ecosystem in northern Sweden, about 200 km north of the Arctic Circle. Stordalen mire (68° 20' N, 19° 03' E, 351 m a.s.l.) is located 10 km east of the Abisko Scientific Research Station (ANS). The mean annual air temperature in Abisko (1913–2003) is -0.7°C . The warmest month is July with a mean air temperature of $+11^{\circ}\text{C}$ (1961–1990, <http://www.ans.kiruna.se>). On a long term basis, 304 mm of precipitation are recorded at this location annually, and the growing season is short (ca. mid May to mid September). The experimental site is characterised by discontinuous permafrost conditions, with slightly elevated drier areas underlain by permafrost and wet, fen-like areas lacking permafrost (Svensson et al., 1999; Johansson et al., 2006; Ström and Christensen, 2007; Bäckstrand et al., 2008). The organic layer at Stordalen is between 1 m and 3 m deep. The vegetation at the mire is dominated by *Eriophorum angustifolium* and *Carex rostrata* in the wet areas, while semi-wet and drier areas, and palsas are dominated by *Eriophorum vaginatum*, *Carex rotrundata* and *Sphagnum* ssp. (Johansson et al., 2006; Bäckstrand et al., 2008).

2.2 Instrumentation and BVOC sampling

The flux measurement system consisted of a sonic anemometer (USA-1, Metek, Elmshorn, Germany) sampling at 20 Hz and a Proton Transfer Reaction-Mass Spectrometer (PTR-MS, Ionicon, Innsbruck, Austria) for online concentration measurements of a set of BVOCs. The PTR-MS uses soft chemical ionisation methods where compounds in the sample air are protonated by H_3O^+ -ions in a drift tube for detection by a quadrupole mass spectrometer. The concentrations of different BVOCs were determined by consideration of the primary ion H_3O^+ (m21), the target BVOC ion count rate and other instrumental parameters according to Lindinger et al. (1998) and Hayward et al. (2002). It has been shown that this results in an accuracy of 30% due to instrument

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and calibration uncertainties (Lindinger et al., 1998; Hayward et al., 2002; Warneke et al., 2003). The PTR-MS has been used for a variety of studies during recent years, including flux measurements of BVOCs above different vegetation types (see reviews by de Gouw and Warneke, 2007; Seco et al., 2007). Detailed information about the PTR-MS can be found in Lindinger et al. (1998).

The sample air inlet for the BVOC concentration measurements was mounted on an eddy covariance mast on Stordalen mire, directly under the scanning volume of the anemometer mounted at a height of 2.95 m agl. The sample air passed through a heated PFA tube (i.d. 8 mm) to the PTR-MS that was operated in a small hut, located 12 m from the flux mast. The air flow from the heated inlet was set to 20 l/min and a sub-sample of 0.3 l/min was taken from the inlet flow and analysed by the PTR-MS.

The drift tube pressure (p_{drift}) of the PTR-MS was kept at 2.2 mbar and the drift tube was heated to $T_{\text{drift}}=60^{\circ}\text{C}$. This led to a kinetic energy of $E/N=130$ Townsend (Td) inside the drift tube. During the vegetation period, the PTR-MS was operated with several different measurement sequences scanning for different sets of BVOC components, including Methanol (m33), Acetaldehyde (m45), Acetone (m59) and Isoprene (m69), with dwell times up to a maximum of 0.5 s each. A typical scanning sequence took about 3 s. During measurements, the instrument background was determined regularly by sampling BVOC-free air, which was filtered by a heated catalytic converter (Zero Air Generator, Parker Balston, Haverhill, MA, USA). Readings of the PTR-MS count rate for the different BVOCs were corrected for the mean daily instrument background values normalized to the count rate of the primary ion m21 during analysis. Based on the standard deviation (2σ) of the background readings and the primary ions, the detection limit of the PTR-MS for the concentration measurements, and thus the signal to noise-ratio (s/n) was calculated. For acetone and methanol the mean s/n was relatively high (18.4 and 9.2, respectively), while mean s/n for acetaldehyde was 3.7. The lowest s/n was found for isoprene, where the measured concentrations exceeded the detection limit only by a factor of 2.2 as a mean value for the whole measurement period. However, taking only data sampled during August, the mean s/n was slightly higher

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(2.8) and thus almost comparable with acetaldehyde, while in September, mean s/n for isoprene dropped down to only 1.4 due to the low ambient concentration. On some occasions the night-time detection limit exceeded the measured values for isoprene, even in August.

To evaluate the long-term stability of the PTR-MS system, measurements of a water cluster ion ($m37$) were used. It is formed between the primary ion and water vapour, and can be used to monitor ambient water vapour pressure (Ammann et al., 2006; de Gouw and Warneke, 2007). Here, the measured $m37$ concentrations (ppb) were converted into absolute water vapour concentration (g m^{-3}), and compared to the water vapour concentration recorded from a temperature and humidity probe at a resolution of 30 min mean values. Over the entire sampling period (1 August to 19 September), this comparison showed a stable linear relationship and a high coefficient of determination ($R^2=0.94$) indicating a good stability of the PTR-MS (Fig. 1).

2.3 Disjunct eddy covariance technique (DEC)

The eddy covariance (EC) technique derives fluxes of energy and mass (e.g. sensible heat flux, latent heat flux, CO_2 flux) made from measurements of turbulence using a sonic anemometer, and trace gas analysers with a typical time resolution of 50 to 100 ms (e.g. Aubinet et al., 2000). However, for compounds like BVOCs, the integration time for the analysis of an air sample usually needs to be longer than 100 ms due to instrument constraints.

The PTR-MS can be used to measure a set of BVOC at a high temporal resolution sequentially, which results in a disjunct time series for the concentration measurements of single BVOCs. For each BVOC included in the measurement sequence, only at N discrete, short time intervals i of length τ (dwell time) measurements of the BVOC concentration c are available. For this disjunct data set, a synchronized sub-sample of the continuously available vertical wind data w was used and the resulting flux F_c was

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calculated according to

$$F_c = \frac{1}{N} \sum_1^N w'(i) \cdot c'(i), \quad (1)$$

where w' and c' are the instantaneous deviations from the mean values of w and c of the sub-sample (Rinne et al., 2001; Karl et al., 2002; Grabmer et al., 2004). Compared to standard EC techniques, this leads to lower measurement frequencies (i.e. 2 Hz) due to longer integration times and significantly fewer data samples (typically ~20% of a continuously recorded data set) depending on the number of different BVOCs sampled in a measurement sequence.

Synchronising of the PTR-MS and the sonic anemometer was ensured by connecting the analogue output of the PTR-MS for ion-counts (cps) and mass identifier to the analogue input of the sonic anemometer. This prevented time-lags caused by different time signals of the recording system and instruments, and the only time lag to be considered was caused by air passing through the tube. To synchronize vertical wind and BVOC concentrations, the turbulent fluxes were calculated for a range of different time lags within the theoretical range estimated from inlet flow and tube dimensions (between 4.0 to 5.0 s) with time steps of 0.05 s. The resulting time series was composed from the maximum absolute fluxes obtained for each of the 30 min intervals separately. For periods where no maximum could be found within the possible range (e.g. at night when fluxes were low) fluxes were calculated with a preset time lag of 4.50 s. This procedure is comparable to that used by Custer and Schade (2007).

To estimate the error of the flux determination, the standard deviation of the covariance of w and c was calculated using time lags in the region of 1 to 1.5 s and 7.5 to 8 s in 0.05 s intervals, which is far away from the time lag used for flux determination (~4.5 s) and regarded as a background (Wienhold et al., 1995; Spirig et al., 2005; Brunner et al., 2007). As a mean value, the estimated error in the flux determination (2σ) was found to be $25 \mu\text{g C m}^{-2} \text{ h}^{-1}$ for isoprene and $19 \mu\text{g C m}^{-2} \text{ h}^{-1}$ for methanol.

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All wind data was rotated along the mean flow and the mean vertical wind velocity (\overline{w}) was set to zero (block averaging with block length of 30 min) (McMillen, 1988). To exclude periods with insufficient turbulence for flux determination, calculated turbulent fluxes were compared against the friction velocity u_* , and flux data with $u_* < 0.25 \text{ m s}^{-1}$ were omitted during analysis.

We focus here on the analysis of BVOC measurements taken with a PTR-MS system during a 50 days period (1 August to 19 September 2006) during the second half of a short growing season at the sub-arctic wetland.

3 Results and Discussion

3.1 Main wind direction and source area

The wind direction frequency distribution showed a two-fold behaviour, with wind frequently from sections NW and SE under both stable and unstable atmospheric conditions (Fig. 2, left). These directions reflect the orientation of the axis of the ca. 10 km broad valley the site is located in. Nevertheless, under stable conditions, a small contribution from SW may possibly be caused by cold drainage flows during night time. The area around the mast that is defined by the main wind sector represents a wet section of the mire, dominated by sedges and with the water table mostly above the surface throughout the growing season. The hut which housed the PTR-MS was located NE (60° to 80°) from the sonic anemometer, and therefore did not disturb the measurements.

For BVOCs like isoprene and methanol the oxidation time under atmospheric conditions is several minutes to hours (Kesselmeier and Staudt, 1999; Singh and Li, 2007), much longer than the period of turbulent transport. To estimate the source area of the measured turbulent fluxes, footprint calculations were done according to Schuepp et al. (1990). The BVOC fluxes measured at the measuring height of 2.95 m agl were dominated by sources at distances of approximately 20 m from the mast (Fig. 2, right).

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For the dominant wind directions, at least 60% of the measured fluxes were emitted within a distance of 100 m from the measurement system. Footprint calculations using the approach based on Wilson and Swaters (1991) resulted in a maximum distance contributing to the measured fluxes of about 50 m for most of the cases, with a maximum of 75 m under stable conditions for certain wind directions (200° to 220°).

3.2 Turbulent fluxes using DEC

Two deviations from standard eddy covariance that characterise the DEC technique may cause an underestimation of the turbulent BVOC fluxes. First, due to the low concentrations of the trace gases being sampled, PTR-MS integration time (also known as dwell time) for each BVOC of interest must be increased to obtain a tolerable signal to noise ratio (s/n). Typical integration times, which are BVOC dependent, are 0.2 and 0.5 s (e.g. Schade and Custer, 2004; Spirig et al., 2005; Lee et al., 2005; Brunner et al., 2007). Second, masses are determined sequentially in the PTR-MS and a number of masses, depending on the BVOCs of interest, are analyzed in a continuously repeating sequence. The time delay between successive measurements of the same BVOC is a function of the number of BVOCs being analysed and the integration time of each. The measurement of the m21 primary ion at the beginning of each sequence increases this delay further still. The sampling constraints outlined above imply that as the number of BVOCs being measured is increased, the number of samples (and hence sample frequency) taken within each 30 min flux calculation period is decreased.

3.2.1 Effect of long integration times

With the DEC set-up, turbulent transport in the high frequency domain (i.e., at a rate >2 Hz) is captured incompletely. The proportion of the high frequency losses can be determined by comparing the sensible heat flux calculated using a full 20 Hz data set of w' and deviations of the mean temperature (T') from the sonic anemometer ($H_{20\text{Hz}}$), with the sensible heat flux calculated from a disjunct sub-set of the same data set

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employing a 0.5 s integration time (H_{disjunct}). By this approach the $w'T'$ subset corresponding to each of the measured compounds used to calculate the BVOC fluxes was taken and compared to the full 20 Hz $w'T'$ time series (Fig. 3). The disjunct data set with its 2 Hz temporal resolution underestimated the turbulent fluxes by approximately 10% due to missing high frequency regions of the spectrum. The coefficients of determination (R^2) were very high, irrespective of the BVOC.

These results were supported by analysing the contributions to the spectral energy for each of the normalized frequency ranges. The spectral data shown in Fig. 4 correspond well with the theoretical shape of turbulence spectra (Kaimal and Finnigan, 1994), with the major part of the flux being transported with larger eddies in the lower frequency range (Grabmer et al., 2004). In comparison to the high-frequency data set with 20 Hz temporal resolution, the disjunct data set missed about 10% of the turbulence energy contained in the high-frequency part of the spectrum. Spirig et al. (2005) found an underestimation of turbulent fluxes due to neglecting high frequency transport of 10.7%, and Lee et al. (2005) assumed the error for sensible heat flux due to the spectral response to be within 10%.

3.2.2 Effect of reduced sample number

The sequential sampling of the PTR-MS reduces the number of samples available to calculate the turbulent fluxes significantly compared to a continuous time series of a single mass. Contrary to the spectral loss of the high frequency part of the spectrum, however, this should have no influence on the calculated fluxes as long as the number of samples within the sample period of 30 min did not fall below a certain minimum. To test this assumption, increasing fractions of the raw data were omitted from a time series of 2 Hz data, which corresponds to integration times of 0.5 s used for the BVOCs in this study. Normalized mean values of $w'T'$ started to deviate significantly from the value calculated from a full data set once the sub-sample fell below 10% of the full data series, above this threshold, the standard deviation of vertical velocity (σ_w) divided by friction velocity (u_*) differed not significantly from that obtained with a full data set dur-

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ing most of the day (Fig. 5, upper panel). Below 5% of the data samples, deviations became much larger and scatter increased notably. Turbulence characteristics, namely (σ_w/u_*) plotted against atmospheric stability (z/L), followed the general patterns suggested by Panofsky et al. (1977) for unstable conditions ($z/L < 0$) and Thomas and Foken (2002) for neutral to stable conditions ($-0.2 < z/L < 0.4$) when at least 10% of the sampled data was used (Fig. 5, lower panel). Overall our analysis indicates that fluxes calculated with less than a fraction of 10% of a full data set would lead to incorrect results. Grabmer et al. (2004) found that the reduction of the samples had virtually no influence on the flux measurement in their study above a Norway spruce forest, and Karl et al. (2002) reported an error based on the disjunct sampling scheme of about 1% of the flux for time scales very similar to those in this study. In our experimental set-up, due to the sequential sampling of the BVOC concentrations, a sub-sample of about 16% of the full data set was used. Since the overall flux loss and precision of the measurements depends on averaging time and sampling interval, measurements are here restricted to not more than six masses.

3.2.3 Damping effects

For variations in BVOC concentrations, damping in the inlet line might occur depending on tube dimensions and flow rate. Although this would reduce the measured fluxes, this effect is considered to be of minor importance compared to spectral losses caused by low sampling frequency (Karl et al., 2002; Spirig et al., 2005; Custer and Schade, 2007). Furthermore, measured BVOC constituents might stick to the walls of the inlet system resulting in an underestimation of fluxes. For example, methanol is known to interact with metal surfaces (de Gouw and Warneke, 2007). Brunner et al. (2007) reported a loss of turbulent exchange due to sorption effects to the wall of the inlet system of 25% to 55% for methanol, depending on wind speed, stating that this effect would be more important than other damping effects. Applying Ogive spectral analysis, Ammann et al. (2006) found high damping for fluxes of the water cluster ion m37, which can be used as a proxy for water vapour pressure. Compared to the un-dampened

sonic temperature measurements, the Ogives are used to estimate damping effects for measured compounds, they describe the cumulative contribution of different frequency ranges to the total turbulent flux. However, as a spectrum can not be calculated from a disjunct time series, this technique could not be used in this study to estimate damping effects. To minimize damping and losses due to sorption effects and to prevent condensation, the inlet line was heated and kept well above ambient temperature in our instrument set-up.

3.3 Meteorological conditions and BVOC concentrations

The study period was characterized by prevailing high pressure conditions and relatively high irradiance during three episodes at the beginning, in the middle, and at the end of August 2006, interrupted by some cloudy days (Fig. 6). In September 2006, the weather was more unsettled. Daily minimum air temperatures close to 2°C were observed frequently towards the end of August, and fell below zero (-0.8°C) on August 20. Daily air temperature maxima exceeded 20°C at the beginning of the measurement period (2 and 3 August), and 17°C on days with high irradiance towards the end of the month. During September, air temperature mostly ranged from about 5°C to 12°C and lacked strong diel variation.

The concentrations of several masses (corresponding to isoprene, acetaldehyde, acetone and methanol) are presented in Fig. 7. A clear diel pattern was observed until early September for isoprene and methanol with maxima reached during the middle of the day when temperature and radiation were high. For acetone and acetaldehyde concentrations did not vary in similarly clear diel pattern but lower frequency fluctuations were observed with concentrations increasing and decreasing over periods of few days.

As could be expected for a high-latitude site, the concentrations were somewhat lower compared to observations in tropical and mid-latitude ecosystems (e.g. Karl et al., 2004; Karl et al., 2005; Custer and Schade, 2007; Brunner et al., 2007), especially for isoprene and acetaldehyde. While the maximum concentrations at Stordalen mire were

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up to 1.2 ppb (isoprene), 6.0 ppb (methanol), 2.1 ppb (acetone) and 0.5 ppb (acetaldehyde), Karl et al. (2004) reported maximum concentrations of ca. 5 ppb (isoprene), ca. 7 ppb (methanol), ca. 2.8 ppb (acetone) and ca. 1.6 ppb (acetaldehyde) measured above a tropical rain-forest, and similar concentrations above a temperate Loblolly Pine plantation (Karl et al., 2005). The atmospheric concentrations at our sub-arctic wetland study site are comparable to values presented for the canopy layer of a boreal mixed forest in south-west Finland measured in July (Rinne et al., 2005), where concentrations between ca. 4 and 6 ppb for methanol, 0.7 to 2 ppb for acetaldehyde, and around 0.5 ppb for isoprene had been recorded. Haapanala et al. (2006) measured isoprene concentrations of approximately 0.8 ppb above a boreal fen in southern Finland.

Concentrations of isoprene and methanol were highest during the daytime at high levels of irradiance ($>1 \mu\text{g C m}^{-3}$ (0.38 ppb) for isoprene and $1.5 \mu\text{g C m}^{-3}$ (2.8 ppb) for methanol). A maximum concentration of isoprene (m69) of $3.2 \mu\text{g C m}^{-3}$ (1.2 ppb) was observed on a comparably hot and sunny day (2 August). Maxima during the rest of the month were about $1 \mu\text{g C m}^{-3}$, but rarely exceeded $0.3 \mu\text{g C m}^{-3}$ on cloudy days. Expressed on a carbon basis, maximum concentrations for methanol (m33) were similar or higher than isoprene, they reached $3.2 \mu\text{g C m}^{-3}$ (6.0 ppb, 1 August), and daily maxima were in the range of 1.5 to $2.3 \mu\text{g C m}^{-3}$ on most other days during the observation period. For other BVOCs, concentration peaks of $3.4 \mu\text{g C m}^{-3}$ (acetone, 28 August) and $0.5 \mu\text{g C m}^{-3}$ (acetaldehyde, 16 September) were observed with means for acetone and acetaldehyde being $1.7 \mu\text{g C m}^{-3}$ (1.0 ppb) and $0.2 \mu\text{g C m}^{-3}$ (0.2 ppb), respectively. Isoprene concentrations dropped to close to zero at night while concentrations of methanol remained at values well above $>0.8 \mu\text{g C m}^{-3}$ (1.5 ppb) with a clear trend of concentration minima declining towards the autumn. In contrast to these diel patterns Rinne et al. (2005) reported concentrations of both isoprene and methanol to peak late in the evening possibly related to high irradiance at the time of measurement (July) at their northern-latitude site.

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3.4 BVOC fluxes

A clear diel pattern for fluxes of isoprene was visible until early September and for methanol during the beginning of August (Fig. 8), whereas no clear diel flux pattern for acetaldehyde and acetone emerged (not shown). The high ambient temperature and high levels of photosynthetically active radiation PAR in early August promoted significant daytime emission of isoprene up to $1385 \mu\text{g C m}^{-2} \text{h}^{-1}$ ($1571 \mu\text{g m}^{-2} \text{h}^{-1}$), while on the following days, isoprene emissions were typically between 400 and $500 \mu\text{g C m}^{-2} \text{h}^{-1}$. At night the measured fluxes for isoprene were close to zero (Fig. 8) as must be expected from the light-dependent foliar production of isoprene and the absence of plant storage for this particular BVOC. In contrast to relatively high emissions during the first half of August, fluxes at the end of the month were less than $250 \mu\text{g C m}^{-2} \text{h}^{-1}$ even during favourable weather conditions. Vegetation at this time of year showed already signs of senescence that began with the frost observed on 20 August ($T_a = -0.8^\circ\text{C}$) and overall low daily minimum air temperature around 2°C . It is likely that air temperature at the actual height of vegetation (ca. 0.5 m) were well below these values that were measured at the eddy tower at a height of 2.5 m. Ekberg et al. (2008) could not detect any isoprene emissions from leaves during a September campaign which corresponds to the observations at ecosystem scale. Overall, the ecosystem isoprene flux increased with temperature and PAR similar to the well-known non-linear pattern observed on leaf scale (i.e. Guenther, 1997; Kesselmeier and Staudt, 1999; Seco et al., 2007) although the response to air temperature was extremely steep at air temperatures above ca. 15°C . At a temperature below this value emissions were close to zero, regardless of incoming PAR (Fig. 9).

In a boreal fen in southern Finland, Haapanala et al. (2006) reported isoprene fluxes varying from 0 to $400 \mu\text{g m}^{-2} \text{h}^{-1}$ measured by relaxed eddy accumulation on a number of days during 2004 (July to October) and 2005 (April to July). Maxima at that site were measured in June and July. A number of other BVOC flux studies in northern wetland ecosystems were conducted with chamber methods (Janson et al., 1999; Hellén et al.,

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2006; Tiiva et al., 2007a,b) and with reported standardized ($1000 \mu\text{mol m}^{-2} \text{h}^{-1}$, 30°C) isoprene fluxes ranging from 70 to $8960 \mu\text{g m}^{-2} \text{h}^{-1}$, measured at ambient conditions and with elevated UV and Ozone levels. The isoprene fluxes presented here confirm an emerging picture whereby emission rates from northern wetlands can be comparable or higher to those observed in boreal forest ecosystems. Janson et al. (1999) stated that a Sphagnum fen emitted isoprene fully comparable to a boreal spruce forest, and Tiiva et al. (2007a) concluded from their studies that isoprene emissions from boreal peatlands are of the same scale as from boreal spruce forests. For sub-arctic peatlands, they found even higher emission rates than reported for forests, especially under warm conditions during summer (Tiiva et al., 2007b). Rinne et al. (2000) observed mean day-time isoprene emissions of $\sim 14.4 \mu\text{g m}^{-2} \text{h}^{-1}$ ($\sim 12.7 \mu\text{g C m}^{-2} \text{h}^{-1}$) for a boreal mixed forest in northern Finland, which is less than the mean emission rate for the Stordalen site for the whole measuring period presented in this study. However, during the Boreal Ecosystem-Atmosphere Study (BOREAS) normalized (20°C , $1000 \mu\text{mol m}^{-2} \text{s}^{-1}$) isoprene emission rates between ca. 600 and $3130 \mu\text{g C m}^{-2} \text{h}^{-1}$ were measured for boreal spruce and aspen forests in Canada during campaigns (spring, summer, late summer) (Fuentes et al., 1999; Westberg et al., 2000). These emission rates exceeded those found for the sub-arctic wetland presented in this study.

For methanol, daytime emissions up to $100 \mu\text{g C m}^{-2} \text{h}^{-1}$ ($268 \mu\text{g m}^{-2} \text{h}^{-1}$) were observed in the beginning of August (Fig. 8). However, from the end of the month onwards fluxes rapidly dropped to values close to the detection limit. Reports on methanol emissions are scarce but our data appear to be within the range of methanol fluxes observed in temperate ecosystems. For grassland, ryegrass and bare soil in central Europe, for instance, Brunner et al. (2007), Custer and Schade (2007) and Schade and Custer (2004) observed fluxes of $\sim 100 \mu\text{g m}^{-2} \text{h}^{-1}$ to $\sim 500 \mu\text{g m}^{-2} \text{h}^{-1}$ ($\sim 38 \mu\text{g C m}^{-2} \text{h}^{-1}$ to $\sim 188 \mu\text{g C m}^{-2} \text{h}^{-1}$), respectively. Our observations suggest methanol deposition occurring during some nights when fluxes of sensible heat were negative, but the flux data were close to the detection limit and the data will require further investigation.

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Isoprene fluxes are frequently analysed using the algorithms and parameterisations of Guenther et al. (1993, 1997) that define emissions by a potential rate (I_s) under standard conditions which varies instantaneously with light in a hyperbolic and with temperature in a modified Arrhenius response. The generally chosen standard conditions when the light and temperature responses are being unity are for an incident quantum flux of PAR=1000 $\mu\text{mol m}^{-2} \text{s}^{-1}$ and a leaf temperature of 30°C. Owing to the cool growth environment at our site, we chose 20°C (air) temperature as reference. The flux data were then used to determine I_s by non-linear curve-fitting (Sigma Plot 9.0, Systat Software Inc.), comparing three cases:

- (a) Using the standard values for the coefficients in the temperature and light response functions as presented in Guenther (1997) (with the temperature response being unity at a reference temperature of 20°C);
- (b) Allowing I_s to vary with average air temperature of the past 48 h (T_{48}) as found at Stordalen mire for the leaf isoprene emission at *Eriophorum* and *Carex* (Ekberg et al., 2008), best described by the dimensionless multiplier $m=a \exp(b T_{48})$;
- (c) Modifying the instantaneous temperature response of I_s in particular the coefficient CT1 (standard value: 95 000 J mol^{-1} ; Guenther et al., 1995).

Agreement between measured data and calculated values was in all cases fairly good, with poorest ($R^2=0.51$) for the Guenther et al. algorithms with the standard setting (Fig. 9, inset). In that case, I_s derived from the non-linear curve-fitting was 329 $\mu\text{g C m}^{-2} \text{h}^{-1}$. The best agreement between measured and calculated isoprene flux ($R^2=0.74$) was achieved when the emission potential I_s was allowed to vary with T_{48} at otherwise standard instantaneous temperature response (Fig. 9, inset), with $I_s=561 \mu\text{g C m}^{-2} \text{h}^{-1}$. Values obtained for parameters a and b in the simple exponential function were 0.07 and 0.14, respectively. On leaf scale, Ekberg et al. (2008) had found similar values for a , but higher value for b (0.21) for a pooled set of normalised data from *Eriophorum* and *Carex* growing near the flux tower. In their analysis, the response

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of the two species was not statistically different, although standardised leaf emissions in *Eriophorum* were overall less responsive to past temperatures. The somewhat lower sensitivity of I_s on ecosystem compared to leaf scale might thus be related to a relatively larger proportion of *Eriophorum* in the footprint of the tower. However, the range of T_{48} in the Ekberg et al. (2008) study, that reports on measurements over two growing seasons was also larger than that encountered during the BVOC canopy flux measurement period, which covered low T_{48} only towards the end. When coefficient CT1 of the temperature response was allowed to vary, agreement of measured vs. fitted data was also improved above the standard values ($R^2=0.73$). In this latter case (c) CT1 was much larger ($225\,000\text{ J mol}^{-1}$) than the original value ($95\,000\text{ J mol}^{-1}$), indicating an extremely steep increase of emissions with temperature. Agreement between model and experimental data could not be improved further by varying any of the other coefficients in the Guenther et al. algorithms.

The estimate of using the Guenther et al. algorithm for I_s (at 20°C) of $323\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ lies within the large range of values reported in other studies (that used 30°C as reference temperature) in boreal fen ecosystems when expressing these for 20°C . For example, Janson et al. (1999) found maximum emission rates of $408\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ (at 30°C and $1000\text{ }\mu\text{mol m}^{-2}\text{ s}^{-1}$) for a *Sphagnum* fen in Sweden, while Haapanala et al. (2006) reported up to $600\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ ($680\text{ }\mu\text{g}$ isoprene $\text{m}^{-2}\text{ h}^{-1}$) for a site in Finland. Hellén et al. (2006) noticed a lower mean isoprene emission potential of $197\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ ($224\text{ }\mu\text{g m}^{-2}\text{ h}^{-1}$) in their study. Tiiva et al. (2007a, b) measured mean standardised emissions varying from $70\text{ }\mu\text{g}$ isoprene $\text{m}^{-2}\text{ h}^{-1}$ to more than $8900\text{ }\mu\text{g m}^{-2}\text{ h}^{-1}$ in microcosms filled with a range of wetland plants and mosses in experiments with ambient conditions tested against elevated UV and Ozone levels. When expressed to be unity at 20°C , these standardised rates range from 17 to $2200\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$. As a mean value for ambient conditions during the growing season, they reported emission rates (normalized to 30°C) of $894\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ ($246\text{ }\mu\text{g C m}^{-2}\text{ h}^{-1}$ at 20°C , Tiiva et al., 2007a).

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Although maximum fluxes of methanol occurred during periods of warm temperatures ($>20^{\circ}\text{C}$) and high levels of PAR ($>750\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$), the correlation of these variables was weak (Fig. 10). Unlike isoprene, emission of methanol is affected by stomatal conductance which may help to explain a short-term co-variation of emissions with assimilation rate (Nemecek-Marshall et al., 1995; Niinemets et al., 2004; Hüve et al., 2007). For grassland in central Europe, Brunner et al. (2007) found a much clearer relation of methanol emission to T_a and PAR; in that study, emissions varied also with assimilation rates. Custer and Schade (2007) reported a temperature-response for methanol fluxes for ryegrass, and in both studies methanol emissions were modelled based on these relationships and leaf area index at the study site. At Stordalen mire, the methanol diel pattern suggests deposition during periods when PAR was very low ($<250\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$) and when $H < 0\ \text{W m}^{-2}$, irrespective of ambient temperatures, although the fluxes measured were close to the detection limit. As methanol is water soluble, condensation and deposition on dew-wetted surfaces or water patches at the wetland site is likely to occur (Seco et al., 2007). This affects not only the diel flux pattern, but also complicates, for example, measurements of water soluble substances with chamber studies (Janson et al., 1999).

Over a season, methanol production is known to be affected by growth and decay of vegetation (e.g. Nemecek-Marshall et al., 1995; Niinemets et al., 2004; Hüve et al., 2007). Similarly, isoprene emissions decline in senescing leaves. The rapid changes in fluxes of isoprene and methanol towards the end of the observation period in autumn can be visualised by comparing mean diel courses from the beginning of August to mid-September. Figure 11 summarises four periods that covered 1 to 5 August (Period I), 10 to 14 August (Period II), 22 to 28 August (Period III), and 12 to 16 September (Period IV). Days were getting visibly shorter towards the end of the period but all selected days were sunny (Fig. 11b) and characterised by relatively similar maximum temperatures (except for Period IV, Fig. 11a).

Isoprene flux maxima tended to coincide with maxima of PAR (Fig. 11b, c) which is also visible in the a strong hysteresis in the isoprene-temperature relationship

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(Fig. 11e). In August, the morning onset of isoprene emission lagged PAR by about 2 h, with fluxes being measurable once PAR exceeded $500 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Fig. 11f). Emissions during Period III reached only about 50% of those measured during Period I or II at similar levels of PAR and T and had ceased during Period IV (by mid-September; Fig. 11c, e, f). Overall, the increase of isoprene emissions with PAR was notably more linear than expected, but PAR at the study site hardly exceeded $1250 \mu\text{mol m}^{-2} \text{s}^{-1}$ and a large proportion of the canopy was below light saturation for most of the day. The linear relationship that seems to be typical for isoprene fluxes and fluxes of sensible heat (Pressley et al., 2005) did also display the effects of decaying vegetation, visible as a strongly decreasing slope in the relationship (Fig. 12). Pressley et al. (2005) reported a gradual increase of isoprene emissions during spring, a significant variation of emissions dependent on light and temperature regimes during summer, and a gradual decline in isoprene emissions in late summer observed during a long-term study in a mixed hardwood forest. Similarly, Westberg et al. (2000) and Fuentes et al. (1999) found a seasonality in the isoprene emission rates for different boreal forest species (black spruce, aspen) during field campaigns at the BOREAS sites, and Fuentes et al. (1999) concluded, that in addition to the seasonality the isoprene emissions of the boreal aspen forest have been strongly reduced by low temperatures ($<10^\circ\text{C}$).

While night-time fluxes of isoprene were virtually zero, the night-time deposition flux of methanol reached ca. $-30 \mu\text{g C m}^{-2} \text{h}^{-1}$. Like for isoprene, a linear relationship with sensible heat flux emerged that also illustrates this nightly deposition (Fig. 12). Morning methanol fluxes peaked notably earlier compared to isoprene (Fig. 11d), saturating at levels of $\text{PAR} > 750 \mu\text{mol m}^{-2} \text{s}^{-1}$ (Fig. 11f). Methanol is stored internally which explains the strong release just after starting stomatal activity in the morning (e.g. Nemecek-Marshall et al., 1995; Niinemets et al., 2004; Seco et al., 2007). Interestingly, the strong seasonal decline visible in peak isoprene rates was not as pronounced for methanol (Figs. 11d, e, f, and 12). Methanol production is often associated with periods of plant growth, but is also emitted from decaying vegetation (e.g. Nemecek-Marshall et al., 1995; Karl et al., 2001; Seco et al., 2007). Over the course of a season these two

processes may compensate each other to some degree resulting in an overall lower seasonal variation.

4 Summary and conclusion

Until now, long-term measurements of BVOCs at a high temporal resolution are scarce, especially in northern latitudes and from non-woody vegetation. In this study, ecosystem-scale measurements of biogenic BVOCs from a sub-arctic wetland, dominated by *Sphagnum*, *Carex* and *Eriophorum* spp. are presented for a period that captured the entire second half of the growing season. For the first time, to our knowledge, we report ecosystem methanol fluxes from a sub-arctic wetland site. Daytime emissions observed were notable (up to ca. $270 \mu\text{g m}^{-2} \text{h}^{-1}$, ca. $100 \mu\text{g C m}^{-2} \text{h}^{-1}$), and deposition appeared to occur at night. Significant emissions of isoprene were observed that were on the same order of magnitude as those published for boreal fens and forests. Standardised to common temperature, our measurements imply that the capacity of northern latitude wetland vegetation to emit isoprene may even be similar to vegetation at much lower latitudes although the strong variation of isoprene emission potential between species make such a simple comparison difficult. Still, from the emerging data from boreal and subarctic ecosystems it appears that the low emissions in these regions are mostly attributable to low temperatures rather to low emission potential per se. For both isoprene and methanol senescence of vegetation played an important role towards the end of the growing season.

BVOC emission responses that were found at leaf scale for the sedges growing at the Stordalen mire study site also emerged at ecosystem scale, namely a rapidly varying emission capacity in response to general weather conditions and a possibly stronger temperature-sensitivity of the fluxes compared to generally used algorithms. The commonly used Guenther et al. temperature relationship has been mostly developed and used in temperate and (sub)tropical ecosystems, and it appears plausible that plants growing in sub-arctic environments may be more sensitive to warm temperatures. More

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data from a wider range of plant species growing in cold-environment ecosystems is necessary to substantiate these observations.

Long-term measurements of BVOC are still lacking for nearly all ecosystems and only very few studies on the seasonal, let alone the interannual variation of BVOC emissions have been published so far. However, such data are required for testing process understanding obtained in laboratory studies and for model evaluation. The data presented here for a sub-arctic mire ecosystem will be useful to support the development, improvement and validation of biogeochemical models to simulate the emission characteristics and ambient level of BVOCs on a regional and global scale under changing climate conditions.

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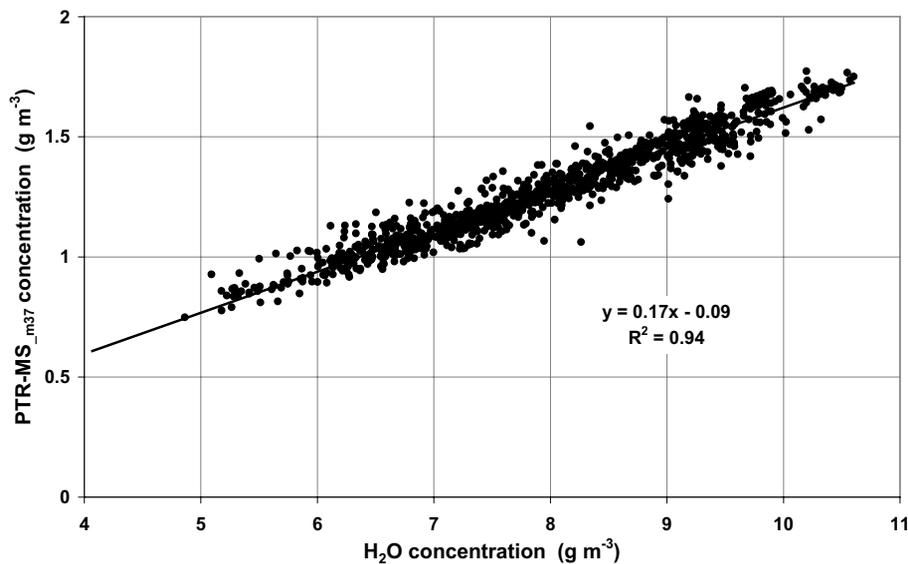


Fig. 1. Comparison of water cluster ion (m37) concentration measurements, expressed as g m^{-3} , and absolute water vapour concentration measured with a standard temperature and humidity sensor covering the period 1 August to 19 September 2006.

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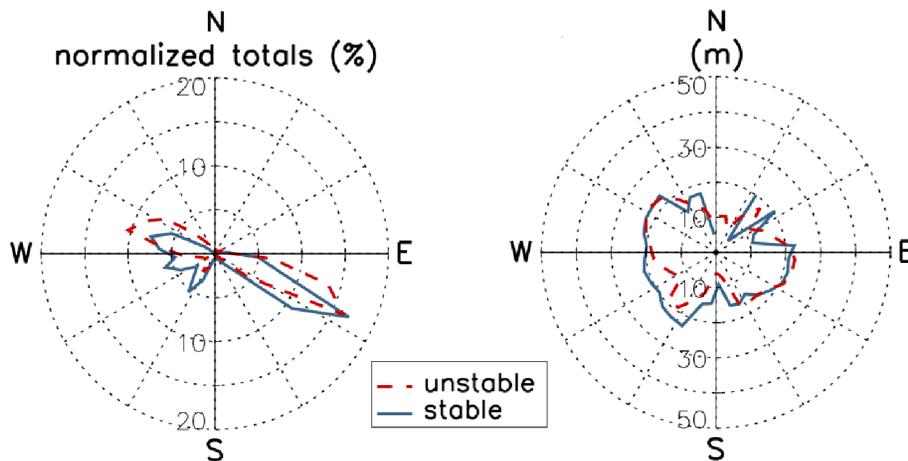


Fig. 2. Frequency distribution (%) of wind direction (left) and footprint according to Schuepp et al. (1990, right) showing the distance that contributed the most to the measured fluxes for stable and unstable conditions measured during August and September 2006.

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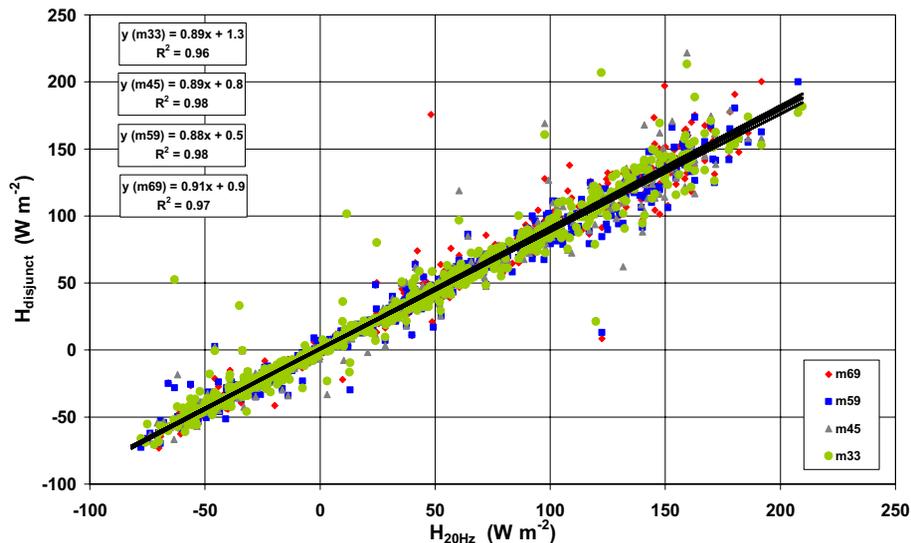


Fig. 3. Comparison of sensible heat flux H , calculated from a full 20 Hz data set ($H_{20\text{Hz}}$) and for a disjunct sub-sample (H_{disjunct}) with 0.5 s integration time as used for VOC sampling. All available 30 min values from August 2006 with $u^* > 0.25$ have been used.

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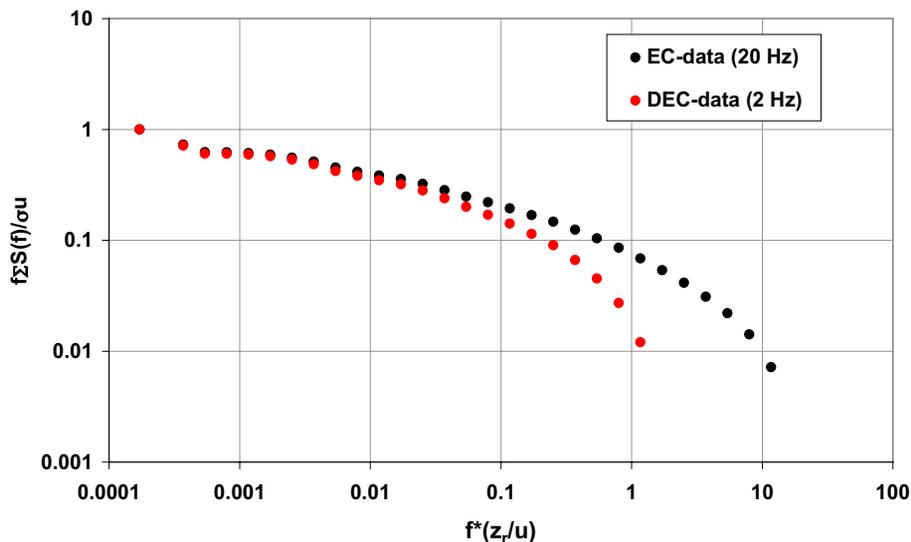


Fig. 4. Cumulative, normalized spectral energy ($f^*\Sigma S(f)/\sigma u$) as a function of normalized frequency ($f^*(z_r/u)$) for two time series of 20 Hz and 2 Hz sampling interval, averaged over the period 1 to 3 August 2006. In this case, about 10% of the spectral energy in the high-frequency range are lost due to the 2 Hz sampling time compared to 20 Hz.

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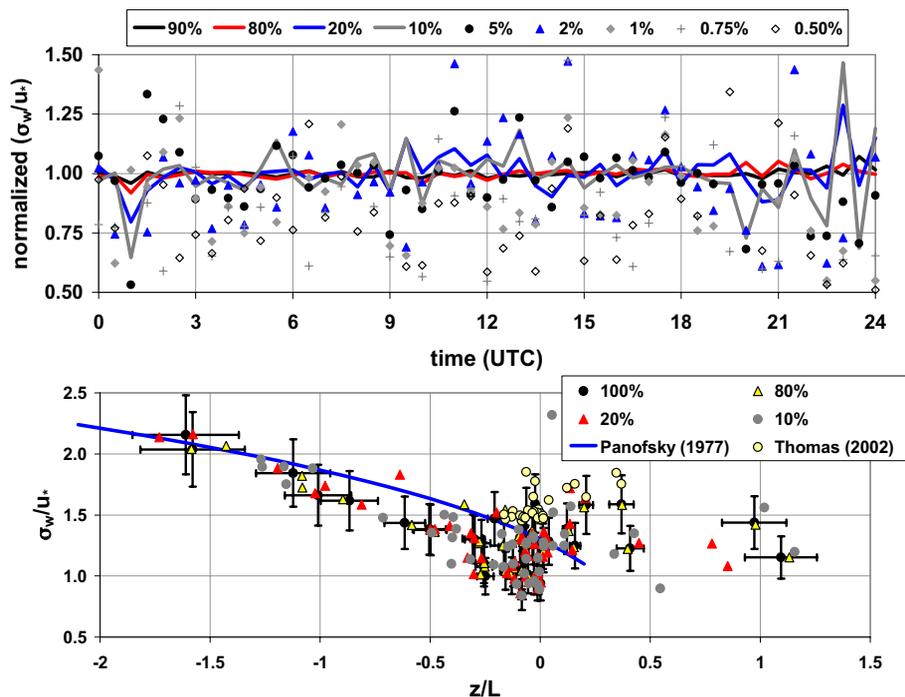


Fig. 5. Comparison of turbulence characteristics (σ_w/u_*) for an exemplary day (4 August 2006). σ_w/u_* calculated from fractions of samples were normalized to the 100% full set for each 30 min file (upper panel). σ_w/u_* against atmospheric stability (z/L , lower panel) agrees well with parameterisations from Panofsky et al. (1977, unstable conditions) and Thomas & Foken (2002, neutral to stable conditions). Error bars for the 100% data show estimated 15% uncertainty.

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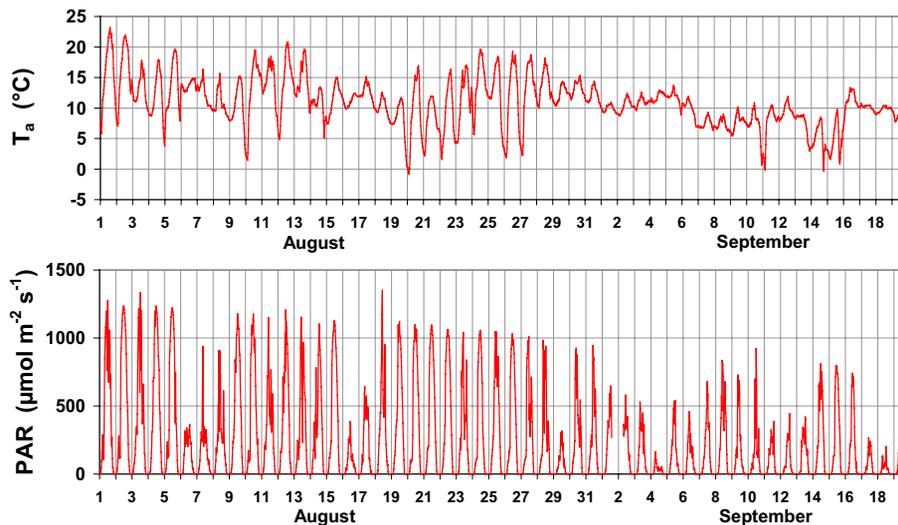


Fig. 6. Ambient air temperature T_a and photosynthetically active radiation PAR measured at the field site Stordalen (northern Sweden) during August and September 2006 (1 August to 19 September 2006).

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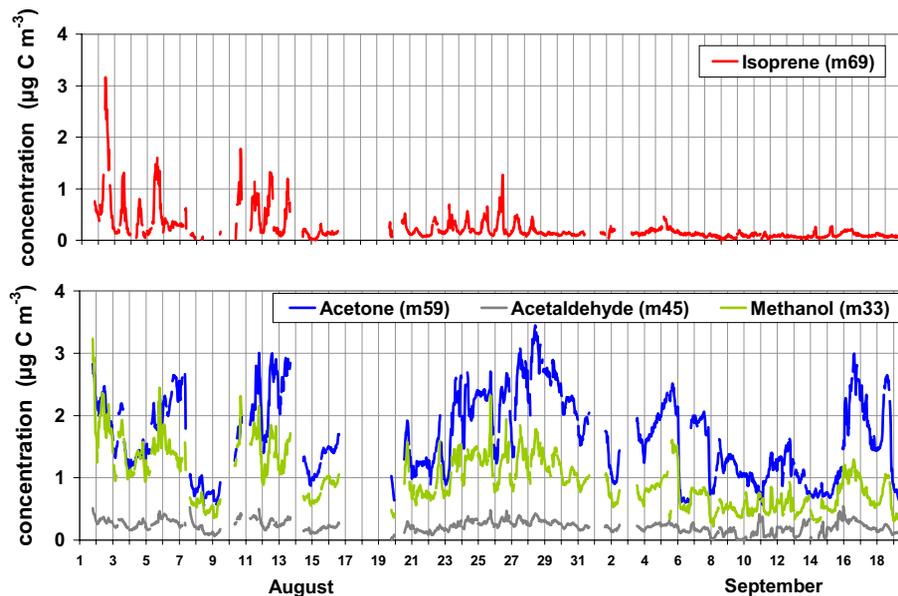


Fig. 7. Concentrations of isoprene, methanol, acetone and acetaldehyde during August and September 2006, measured by a Proton Transfer Reaction mass spectrometer (PTR-MS) at a height of 2.95 m above Stordalen mire in northern Sweden.

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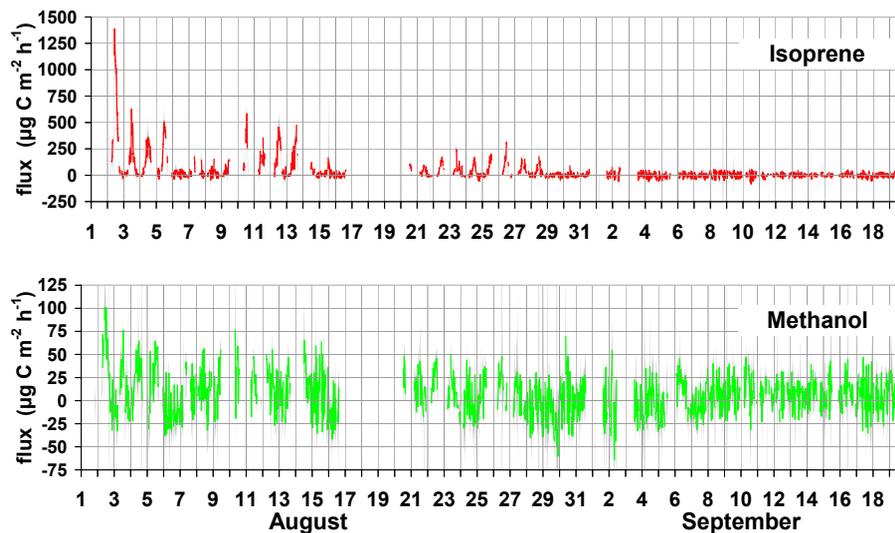


Fig. 8. Ecosystem exchange of isoprene (top) and methanol (bottom), measured at a sub-arctic site in northern Sweden during August and September 2006. Grey shading indicates fluxes ± 2 standard deviations of the background signal of the fluxes.

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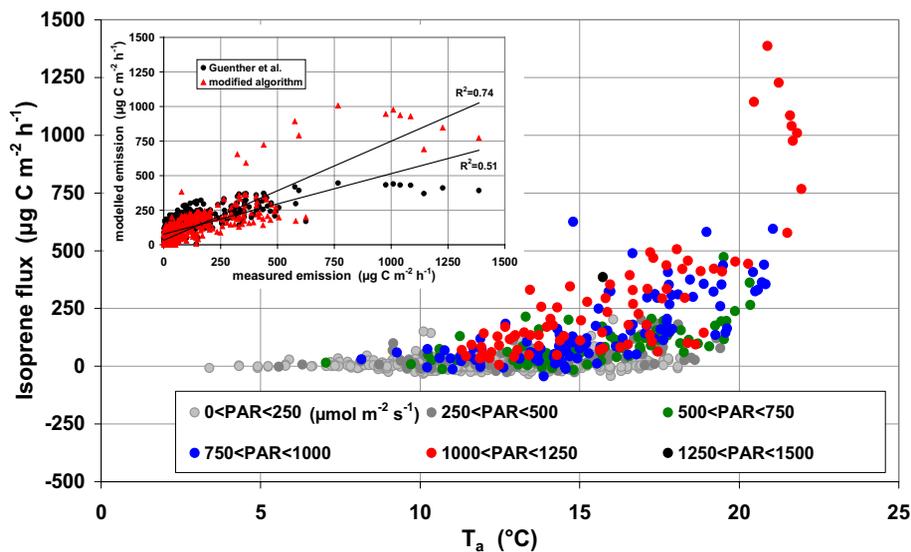


Fig. 9. Measured fluxes of isoprene related to ambient air temperature T_a and ambient level of photosynthetically active radiation (PAR, colour coded) for August 2006 as well as measured isoprene emission compared with emission modelled with two different approaches. The inset shows measured values vs. values from a non-linear curve fit against the measured data. Black symbols denote results using the standard Guenther et al. algorithm, red symbols show fitted data with f_{s20} varying additionally in response to average temperature over the last 48 h.

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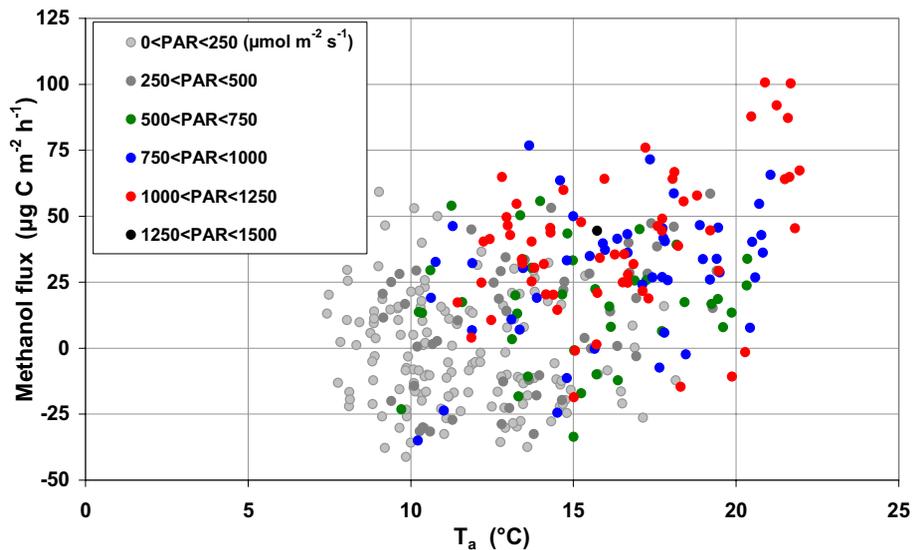


Fig. 10. Measured fluxes of methanol related to ambient air temperature T_a and ambient level of photosynthetically active radiation (PAR, colour coded) for the first half of August 2006 (1–16 August).

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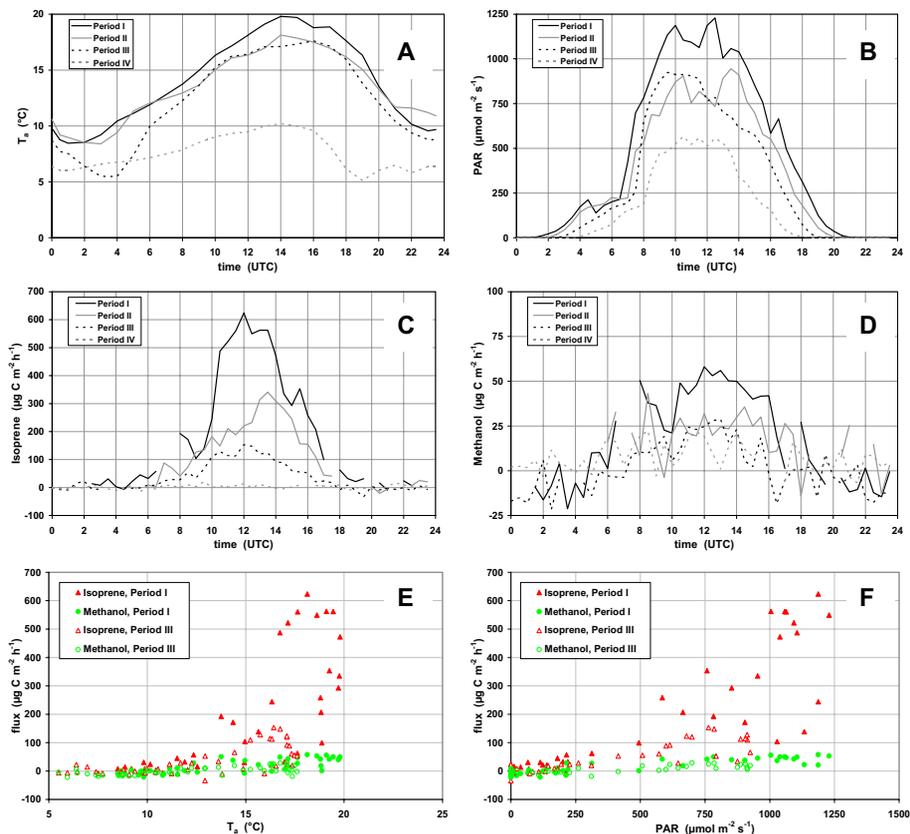


Fig. 11. Mean diel courses for ambient air temperature T_a , photosynthetically active radiation PAR, and turbulent fluxes of isoprene and methanol for different periods (period I: 1/8–5/8; II: 10/8–14/8; III: 22–28/8, and IV: 12/9–16/9) during 2006 as well as mean diel courses of fluxes of isoprene and methanol related to T_a and PAR for two contrasting periods (I, III).

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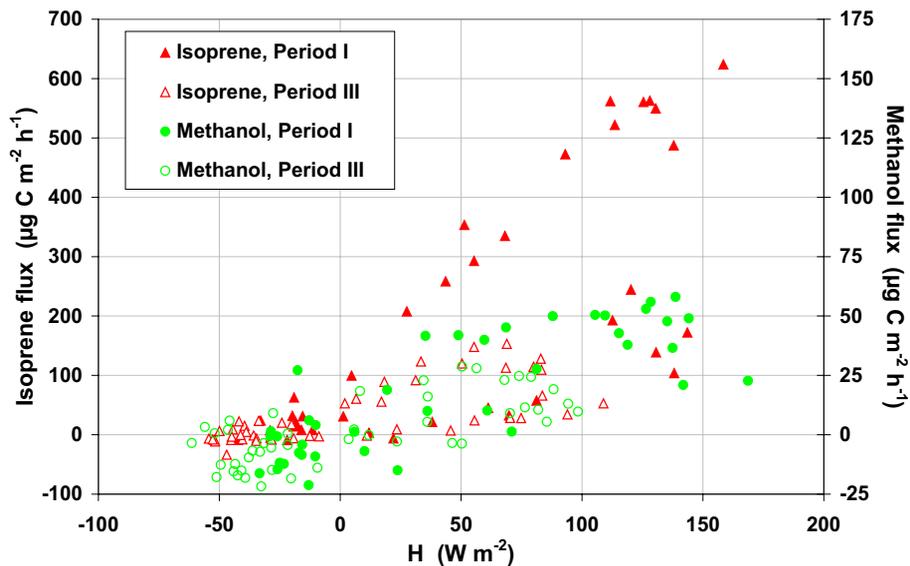


Fig. 12. Mean diel courses of fluxes of isoprene and methanol in relation to mean sensible heat flux H for two contrasting periods (I: 1/8–5/8; III: 22/8–28/8) during the 2006 field season.

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