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On-line PTR-MS measurements of atmospheric concentrations of volatile organic compounds in a European boreal forest ecosystem

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On-line measurements of atmospheric VOC concentrations in the European boreal zone with a proton transfer reaction mass spectrometer were conducted at SMEAR II station in Hyytiälä, south-western Finland on 2–22 July 2004. The measurements showed a strong diurnal variation of several compounds. A factor analysis performed for the concentration data was used to classify the measured VOC masses into three classes based on the behavior of their concentrations. The masses in the first class had a high diurnal variation with maximum values in the afternoon. Compounds contributing to masses in this category were e.g. methanol, acetone, methyl-vinyl-ketone and hexanal. The concentrations of masses in the second class had also a high diurnal variation, but with maxima during the night when the mixing of the atmospheric surface layer was weak. Monoterpenes and phenol are compounds contributing to the masses in this category. The masses in the third class did not have a marked diurnal cycle and were not dependent on the local meteorological parameters. The masses having a strong positive loading on this factor were those associated with anthropogenic compounds with relatively long atmospheric life-times, such as benzene. Considering the difference in the measurement height, the total monoterpene concentration measured by the PTR-MS was consistent with the concentration measured by gas chromatography-mass spectrometer with adsorbent sampling.

Introduction

Boreal forests are one of the major vegetation types on Earth, covering about 10% of the land surface. In Eurasia, the boreal zone, or Taiga, extends from Scandinavia through Siberia to the Pacific coast. As the boreal regions are typically sparsely populated, the emissions of volatile organic compounds (VOCs) are dominated by biogenic sources (e.g. Simpson *et al.* 1999, Lindfors *et al.* 2000). As a consequence, in the remote boreal regions the reactivity-scaled concentrations of biogenic VOCs (BVOCs) dominate over the anthropogenic VOCs (AVOCs) (Hakola *et al.* 2000). Also on the global level the VOC emission is dominated by biogenic sources (Müller 1992, Guenther *et al.* 1995).

Concentrations and emissions of VOCs in the European boreal region have previously been studied mainly with methods based on canister and adsorbent sampling with subsequent laboratory analysis (e.g. Isidorov *et al.* 1985, Janson 1993, Laurila and Hakola 1996, Hakola *et al.* 1998, 2000, 2001, 2003, Janson *et al.* 1999, Rinne *et al.* 1999, 2000a, 2000b, Spanke *et al.* 2001, Hellén *et al.* 2004). These methods work well, for example, for the isoprene and monoterpene analysis. However, it is estimated that these compounds make only about half of the biogenic VOC emissions both globally and from the European boreal regions (Guenther *et al.* 1995, Lindfors *et al.* 2000). In the other half there exist many compounds, such as many oxygenated VOCs, for which the sampling methods do not work very well.

The off-line analytical techniques are also time-consuming, whereas the on-line analysis of VOCs enables continuous measurements of concentrations and emissions. The time series created by such methods enable closer analysis of the mechanisms controlling the VOC concentrations in the atmosphere.

The proton transfer reaction-mass spectrometry (PTR-MS), which is a form of chemical ionization mass spectrometry, has been developed into a state-of-the-art measurement technique for VOCs at the ambient concentration levels (Lindinger *et al.* 1998a, 1998b). Recently PTR-MS technique has been used to measure both concentrations and emissions of VOCs, including the oxygenated VOCs (e.g. de Gouw *et al.* 1999, Karl *et al.* 2001, Warneke *et al.* 2002, Ammann *et al.* 2004). One of the advantages of the PTR-MS technique is its fast response time together with high sensitivity, which enables flux measurements of VOCs by an eddy covariance method (Karl *et al.* 2001, 2002, Rinne *et al.* 2001). This technique has not been used to measure VOCs in the European boreal regions before. Recently chemical ionization mass spectrometry (CIMS), based on ion molecule reaction, was used for the measurement of VOCs in the boreal forest by Sellegri *et al.* (2005).

During the summer of 2004 first on-line measurements of concentrations of VOCs in a European boreal forest ecosystem with a PTR-MS were conducted at SMEAR II. Results of these measurements are presented in this paper. The dominant tree species at the site of the measurements reported here is Scots pine (*Pinus sylvestris*). These trees are reported to emit monoterpenes, of which α-pinene and Δ^3-carene are the dominant ones (Janson 1993, Janson and de Serves 2001), as well as acetone, acetaldehyde and formaldehyde (Janson and de Serves 2001). Norway spruce (*Picea abies*), dominant in some areas near the measurement site, is reported to emit also monoterpenes, dominantly α-pinene and limonene, and acetone, but also isoprene (Janson and de Serves 2001). These two tree species are also the dominant tree species in Finland, and their emissions are likely to dominate the biogenic VOC emissions into the atmosphere from Finland.

Measurements

The measurements were carried out at the SMEAR II measurement station (Station for Measuring Forest Ecosystem–Atmosphere Relations) of the University of Helsinki in Hyytiälä, southern Finland (61°N, 24°E, 180 m above sea level). The forest around the station is dominated by Scots pine (*Pinus sylvestris*) with some Norway spruce (*Picea abies*), European aspen (*Populus tremula*) and birch (*Betula pendula* and *pubescens*). The Scots pine forest was planted in 1964. A commercial thinning was conducted at the site in 2002. In this thinning smaller trees and seedlings were removed to give the larger trees more space (Vesala *et al.* 2005).

At the SMEAR II station an extensive set of year round measurements of forest–atmosphere interactions is conducted. These measurements include eddy covariance fluxes of heat, H_2O, CO_2, O_3 and aerosol particles (Suni *et al.* 2003), relaxed eddy accumulation measurements of size resolved particle fluxes (Gaman *et al.* 2004), and profile measurements of CO_2, O_3 and NO_x (Vesala *et al.* 1998). Gas exchange between the atmosphere and plants or soil is measured also with automated and manual chambers (Hari *et al.* 1999).

In the PTR-MS method the primary hydronium ion (H_3O^+), used to ionize the target compound, is generated from water vapor by hollow cathode discharge in the ion source. The target compound to be measured (R) is then ionized by a proton transfer reaction with hydronium ion,

$$H_3O^+ + R \longrightarrow H_2O + RH^+ \qquad (1)$$

to yield the water molecule and ionized target molecule which has molecular mass one atomic mass unit (amu) higher than the original target molecule. For a proton transfer reaction to occur the target compound must have a higher proton affinity than the water molecule. This is the case for a wide variety of interesting compounds. A more detailed description of the PTR-MS technique is given by Lindinger *et al*. (1998a, 1998b).

The proton transfer reaction is a relatively gentle ionization method. Many compounds such as methanol and isoprene do not fragment in this method. However, many compounds with higher molecular mass do fragment. The fragmentation patterns were studied for example by Tani *et al*. (2003, 2004). Since the exact pattern of fragmentation depends on the settings of the PTR-MS, mainly the reaction chamber pressure and voltage (E/n ratio), the published fragmentation data must be used with care.

The ionized target compound, which is selected by mass using a quadrupole mass filter, is detected by a secondary electron multiplier. As the target compound is selected only by its mass, the PTR-MS does not distinguish between different compounds with the same mass. Thus for example monoterpenes can not be distinguished from each other.

The PTR-MS used at the SMEAR II is capable of measuring concentrations with a time response shorter than one second. However, to reduce the noise in the concentration measurement due to the counting statistics, integration times between 1 and 20 seconds were used for single measurement. The longest integration times were used for compounds with lowest concentrations.

The VOC concentrations were measured with the PTR-MS below the forest canopy at two meters above the ground. The sample air was drawn in via two-meter-long 1/8´´ Teflon® tubing. Totally 39 masses were measured, ranging from 31 to 205 amu. The measurement cycle length was about four minutes. The masses measured, for which information on the compounds contributing to their concentrations is available, are listed in Table 1. As the PTR-MS cannot distinguish between compounds with the same mass and thus can not be used for identification of measured compounds, the compounds associated

Table 1. Selected masses measured by the PTR-MS with compounds contributing to their concentrations.

Protonated mass (amu)	Contributing compounds	Integration time (s)
33	Methanol	1
41	Hexanol fragment	10
42	Acetonitrile	5
43	Propene, Hexanol fragment	1
45	Acetaldehyde	1
47	Formic acid, Ethanol	1
57	Hexanol fragment, Hexenal fragment	10
59	Acetone	1
61	Acetic acid	1
63	Di-methyl-sulfide (DMS)	5
69	Isoprene	5
71	Methyl-vinyl-ketone (MVK), Methacrolein	10
73	Methyl-ethyl-ketone (MEK)	10
75	Butanol	10
79	Benzene	10
81	Monoterpene fragment	5
82	Limonene fragment	10
87	2-Methyl-3-Buten-2-ol (MBO)	5
93	Toluene	10
95	Phenol	10
99	Hexenal	10
101	Hexanal	5
107	Xylene	10
137	Monoterpene	10

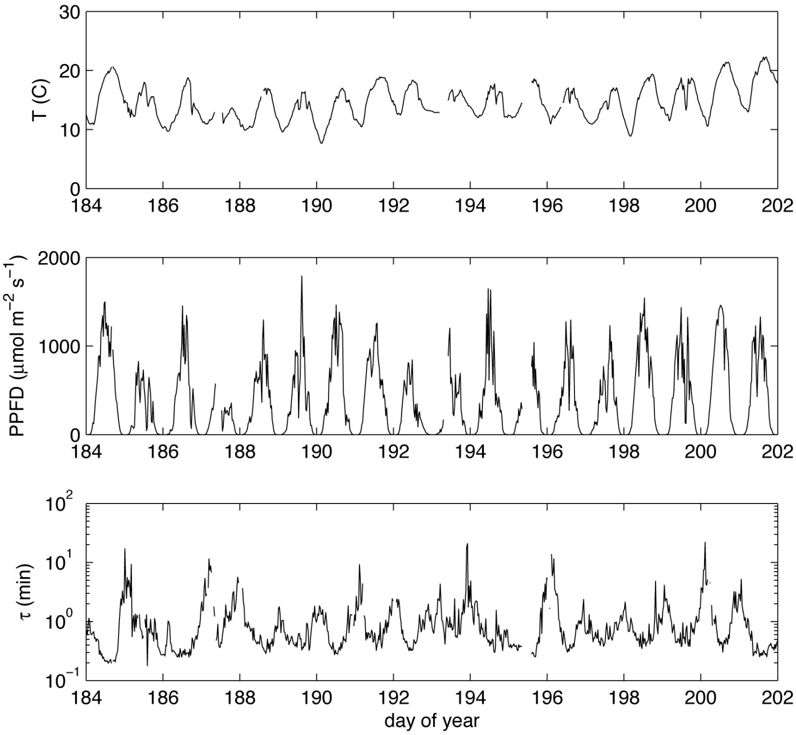

Fig. 1. Meteorological data during the concentration measurements: Temperature at 17 m (T), photosynthetical photon flux density (PPFD) and turbulent mixing time-scale for measurement height of 23 m ($\tau = z_m/u^*$). On the *x*-axis is the day of the year with tick marks at midnight.

with masses in this paper are only the most likely candidates. The below-canopy concentrations were measured during 2–20 July 2004.

Also vertical profiles were measured during two days (21 and 22 July) with the gas profiling system existing at the SMEAR II station. In this system air is brought down from six heights (4, 8, 17, 34, 50, 69 meters), using Teflon® tubing of equal length, with 14 mm inner diameter. The flow rate in these tubes is 50 l min^{-1} and sample flow to analyzers is taken as a side flow with electronic valves. Each height is measured one minute at a time, leading to a six minute cycle. The signal of the valve switching relays was used to trigger the PTR-MS sampling cycle, which measured count rates of 15 masses within less than one minute.

Concentrations of a measured compound ([R]) were calculated with the following equation:

$$\left[\mathrm{R}\right] = \frac{1}{kT_r m}\frac{\left[\mathrm{RH}^+\right]}{\left[\mathrm{H_3O}^+\right]_0} \qquad (2)$$

where $[\mathrm{H_3O^+}]_0$ is the primary ion count rate in the absence of reactive compounds, k is the proton transfer reaction rate (2×10^{-9} cm^3 s^{-1} was used for all masses) and T_r is the average time the ions spend in the drift tube, and $[\mathrm{RH^+}]$ is the count rate of the protonized target compound. We determined, for the calculation, the mass dependent detection efficiency (m) of the measured molecules and fragmentation pattern of monoterpenes, other compounds were considered not to fragment. The zero air count-rates were not measured during the field measurements but afterwards using a catalytic zero-air generator (Parker ChromGas Zero Air Generator, Model 1000).

VOCs in the ambient air are routinely sampled at the SMEAR II station using adsorbent techniques with subsequent laboratory analysis. During summer 2004, four or more samples were taken each month above the forest canopy at the height of 20 m. The sampling time was 60 minutes and the flow rate was about 70 sccm min^{-1}. The samples were analyzed by the Finnish Meteorological Institute by GC-MS technique as described by Hakola *et al.* (2003).

Results and discussion

Parameters describing the local meteorology are presented in Fig. 1. The daytime temperatures

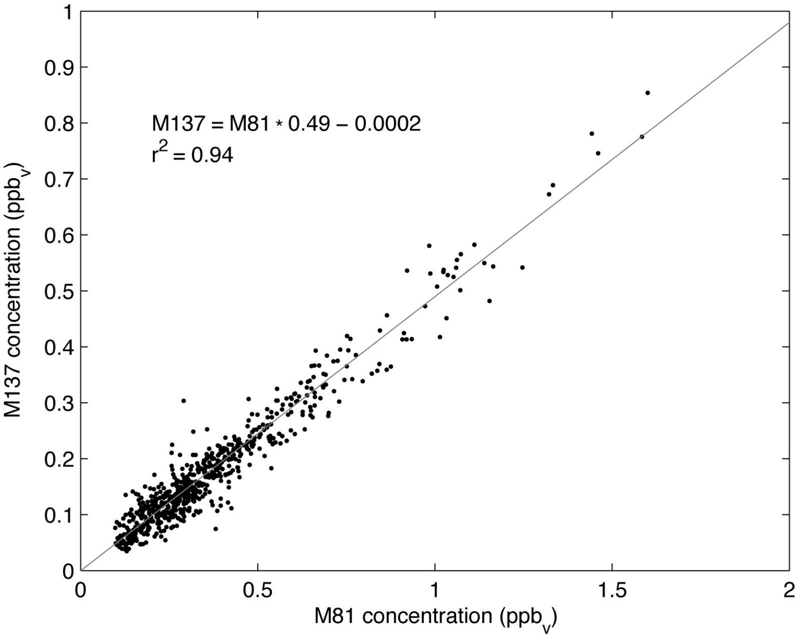

Fig. 2. Half-hour average concentration of protonated monoterpene mass M137 against that of monoterpene fragment M81. The gray line shows their relation as described by the linear equation and correlation coefficient in the figure.

were mostly around 20 °C during the measurement period. The PPFD was generally above 1200 μmol m^{-2} s^{-1} with a couple of more cloudy days. The mixing time scale, $\tau_{u*} = z_m/u*$, where z_m is the measurement height above the zero displacement height and $u*$ the friction velocity, had highest values up to ten minutes during night due to the low turbulence. The daytime mixing times were shorter than one minute. As the height z_m refers to the height of the turbulence measurements conducted above the canopy, the mixing time-scale refers to the above-canopy mixing.

An example of the fragmentation in the PTR-MS is the fragmentation of monoterpenes, with protonated mass of 137 amu. Monoterpenes fragment in the PTR-MS to yield a positive ion with mass of 81 amu, but the exact ratio of fragmentation depends on the monoterpene in question and the ratio of electric field to the gas density (E/n) in the drift tube (Tani *et al.* 2003, 2004). Tani *et al.* (2003) studied the fragmentation of α-pinene and Δ^3-carene with E/n ratios between 80 and 120 Td, and observed the ratio of M137 to M81 to decrease when increasing the E/n ratio. Limonene was found to fragment also into M82 by Tani *et al.* (2003). During the measurements reported here the E/n ratio was 130 Td. Correlation between the monoterpene masses M137 and M81 is shown in Fig. 2. It can be seen that the relation between these masses is linear with M137 to M81 ratio of 1:2 and the correlation coefficient $r^2 = 0.94$.

A factor analysis was performed on the half-an-hour averages of measured concentrations to classify the masses with similar behavior. The compounds included into the factor analysis were all the masses listed in Table 1. Also included in the factor analysis were the environmental parameters: ambient temperature, photosynthetical photon flux density (PPFD), mixing time-scale and ambient water vapor mixing ratio. The concentration data as well as the meteorological data were standardized with respective standard deviations. Earlier Laurila *et al.* (1999) used the factor analysis to study the seasonal behavior of the concentrations of C_2–C_5 hydrocarbons in the European boreal region. The data used in their study was from canister samples taken twice a week in the afternoon and revealed the behavior of isoprene concentration to be different from other C_2–C_5 hydrocarbons.

The masses measured were divided into three classes by factor analysis as the solution with three factors proved to be most insensitive for removal of any two-day period of data. The resulting factor loadings are shown in Fig. 3. Masses which had high loading on factor 1 include M33 (methanol), M71 (methyl-vinyl-

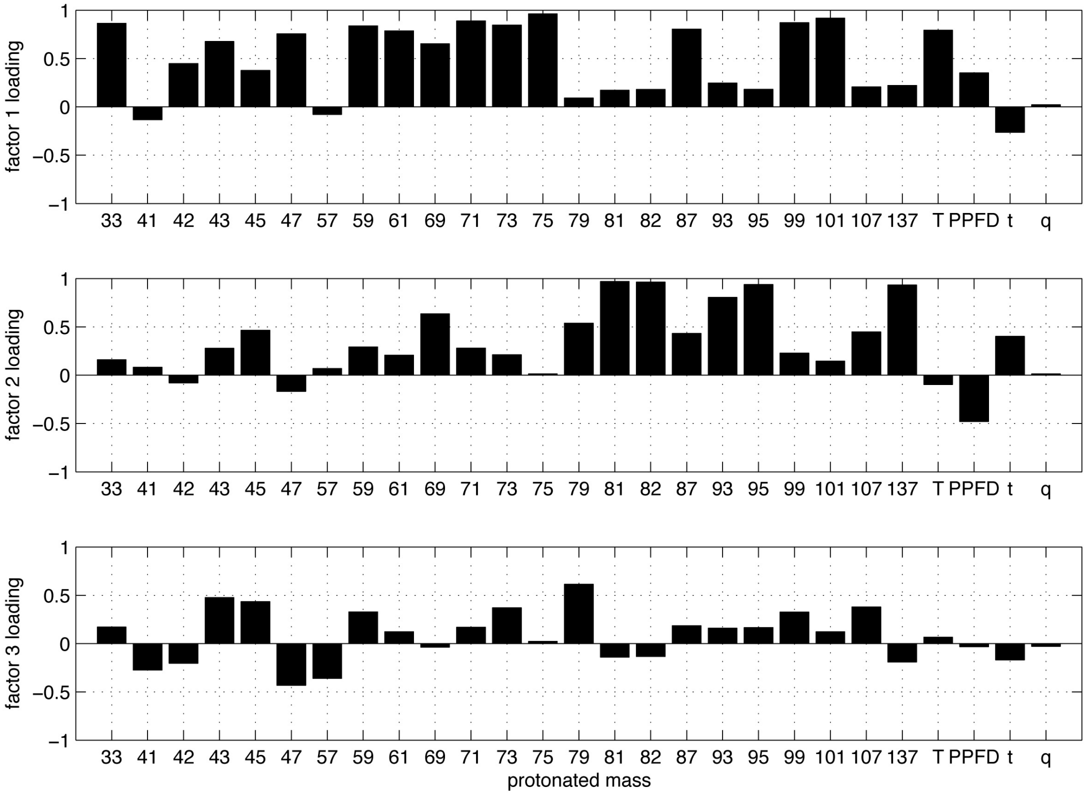

Fig. 3. Results of the factor analysis with three explaining factors. On the *x*-axis are measured masses and ambient air temperature (*T*), phosynthetical photon flux density (PPFD), mixing time-scale (*t*) and ambient water vapor mixing ratio (*q*).

ketone, methacrolein) and M73 (methyl-ethyl-ketone). Also air temperature and photosynthetical photon flux density (PPFD) had relatively high positive loading on factor 1. As these two meteorological parameters are strongly correlated with each other on a diurnal time-scale, the individual contribution of the parameters is difficult to separate. The compounds having high loading on factor 1 have local sources. Many of them have biological sources but some are emitted by anthropogenic activity (M75, butanol) and some have chemical sources (M73, MEK). Water vapor mixing ratio had nearly zero loading on this or any other factor and, thus, does not explain diurnal variations.

M81 (monoterpene fragment) and M137 (monoterpene) had a high loading on factor 2. Also M93 (toluene) and M95 (phenol) had high factor loadings on factor 2. Of the environmental variables, the mixing time-scale had positive loading on factor 2 indicating effect of turbulent mixing to the concentrations. As the mixing time-scale and incoming solar radiation are anticorrelated, the PPFD had negative loading on factor 2. The monoterpene emissions from Scots pine have been observed to depend on temperature and not on PPFD (Janson 1993). The much stronger diurnal cycle of mixing time-scale as compared with that of emission forced by temperature leads to accumulation of monoterpenes in the nocturnal surface layer. The high factor loading on factor 2 of M82 and M95 indicate that the concentrations of the compounds contributing to these masses are affected by similar processes. The very high factor loading on factor 2 of M82 indicates that limonene is the compound mostly contributing to the measured concentration of M82.

In factor 3 the local environmental parameters had nearly zero factor loadings. M45 (acetaldehyde) and M79 (benzene) had the highest positive loading, whereas M47 (formic acid and

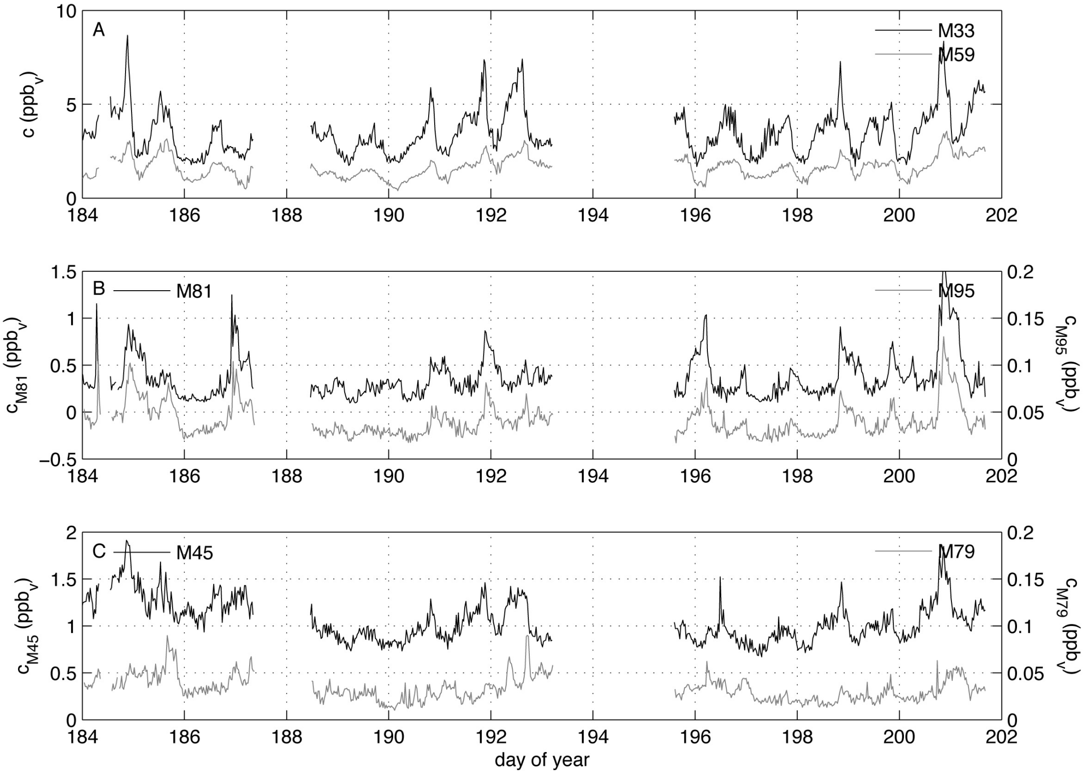

Fig. 4. Time series of half-an-hour average concentrations (*c*) of selected compounds in the sub-canopy atmosphere. Panel **A** shows concentrations of masses having high loading on factor 1, panel **B** on factor 2, and panel **C** on factor 3. The data are presented as half-an-hour averages and on the *x*-axis is the day of the year with tick marks at midnight. Note the different scales for the two compounds in the lower two panels.

ethanol) had strong negative loading. All these have relatively long atmospheric life-time. Benzene is associated with anthropogenic sources.

The masses with high loading on factor 1, such as M33 (methanol) and M59 (acetone) shown in Fig. 4A, generally showed highest concentrations in the late afternoon and lowest concentrations during early morning hours. Here 2.5 ppbv was subtracted from the concentration calculated with the Eq. 2, as the zero-air test using a catalytic zero air generator showed background count rate yielding this concentration. The masses having high loading on factor 2, such as M81 (monoterpene fragment) and M95 (phenol), showed highest concentrations at night, when turbulent mixing is less efficient, and lower concentrations during the daytime (Fig. 4B). The compounds having high loading on factor 3 did not show a strong diurnal cycle. As examples, M45 (acetaldehyde) and M79 (benzene) are shown in Fig. 4C.

Two daily cycles of vertical concentration profiles of M33 (methanol), M69 (isoprene) and M81 (monoterpene fragment) with meteorological parameters measured on 21 and 22 July are shown in Fig. 5. Weather during these days was sunny as can be seen on the PPFD measurements. M33 and M81 showed higher concentrations near the surface during daytime especially on 22 July indicating a surface source. In spite of having a clear diurnal cycle M69 did not exhibit such a clear vertical daytime gradient. This indicates the lack of isoprene emitting tree species in the flux footprint area. Night-time accumulation of M81 near the surface could be clearly seen, as monoterpenes were emitted also during night-time. The diurnal cycle of the concentration of M81 at the lowest levels tracks the mixing time-scale closely. This can also be seen in Figs. 1 and 3, although in the longer term other factors, such

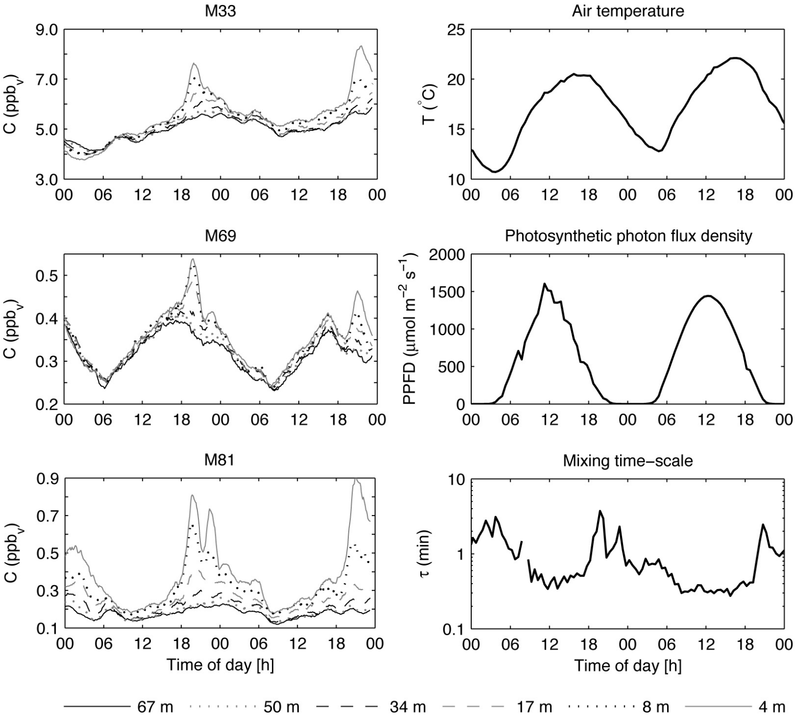

Fig. 5. Vertical profiles of M33 (methanol), M69 (isoprene) and M81 (monoterpene fragment), together with meteorological parameters: air temperature at 17 meters, photosynthetical photon flux density (PPFD) and turbulent mixing timescale for measurement height of 23 m ($\tau = z_m/u^*$).

as changes in ambient temperature and changes in the emission potential, play a relatively bigger role. In contrast to the results from adsorbent sampling below the canopy at the same site presented earlier by Rinne *et al*. (2000a), the daytime concentrations of M81 below the forest canopy are only moderately higher than the concentrations above the canopy. This could be partly explained by the thinning of the forest in 2002 (Vesala *et al*. 2005) which may have lead to increased below-canopy mixing.

Methanol, contributing to the M33, is commonly the dominant oxygenated hydrocarbon in the rural atmosphere (e.g. Fehnsenfeld *et al*. 1992). Its main source into the atmosphere is estimated to be vegetation, but having also other sources, such as methane oxidation, plant matter decay, biomass burning and anthropogenic sources (Heikes *et al*. 2002). The emission of methanol from plants is higher from growing leaves than from mature ones and conifers tend to have lower methanol emission than broadleaved plants (MacDonald and Fall 1993). Methanol is emitted mainly through the stomata and thus controlled by the stomatal conductance (Nemecek-Marshall *et al*. 1995). The diurnal cycle of M33 concentration observed at SMEAR II can be explained by the emission pattern of methanol. Following the opening and closure of the stoma, the emission would follow the diurnal cycle of PPFD leading to afternoon maxima in the surface layer concentration.

Jacob *et al*. (2002) estimated that the most important sources of acetone, contributing to the M59, include emission from vegetation, oxidation of isoalkanes and a photochemical ocean source. Scots pine, the dominant tree species at the measurement site, as well as the Norway spruce (Janson and de Serves 2001) which is the other dominant tree species in Finland, has been reported to emit acetone. As the concentrations of M59 and M33 have both high factor loading on factor 1, and as their diurnal cycles follow each other closely, it seems that the surface layer concentrations of these compounds are dominated by the same processes.

Diurnal cycle of M69 (isoprene) showed the sub-canopy concentration generally increasing during the daytime, with peak concentrations often just before midnight, and decreasing at night (Fig. 6). This behavior is similar to previous measurements of M69 at SMEAR II by

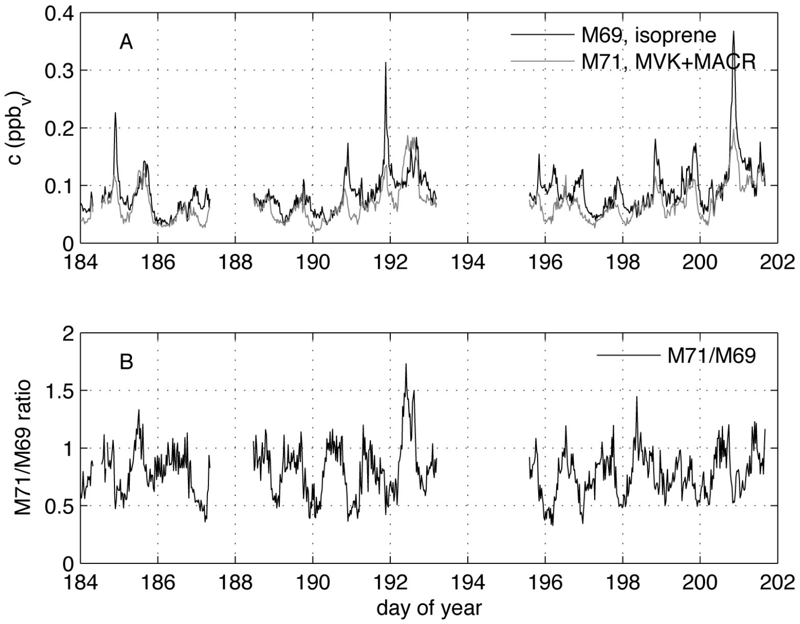

Fig. 6. Concentrations of M69 (isoprene) and M71 (methyl-vinyl-ketone, MVK + methacrolein, MACR) and their ratio in the sub-canopy atmosphere. The data are presented as half-an-hour averages and on the *x*-axis is the day of the year with tick marks at midnight.

CIMS technique (Sellegri *et al.* 2005) but differs from that reported by e.g. Ammann *et al.* (2004), who measured M69 concentrations above a mid-latitude deciduous forest to have the highest values in the afternoon and lowest after midnight. The reason for this difference may lie in the differences in the light environment between the mid-latitudes and northern latitudes. The light and temperature conditions at Hyytiälä late in the afternoon and early evening during the measurement period may have been sufficient to sustain continuing isoprene emissions, the PPFD was about 500 μmol m^{-2} s^{-1} and air temperature around 20 °C at 6 pm (Fig. 5). During daytime, the high reactivity of isoprene with OH in particular, as well as the daytime mixing, results in low daytime concentrations. If there is enough light for isoprene emissions to continue until late in the afternoon and evening, the concentrations may very well increase, build up due to decreased reactivity and decreased mixing. The lack of strong isoprene emitters in the vicinity of the measurement site is also in contrast with that of Ammann *et al.* (2004) with abundant isoprene emitting oaks. Also the different position of sample intake may have an effect on the diurnal behavior of isoprene concentration, as the concentrations above the canopy at SMEAR II had the concentration maxima earlier (Fig. 5).

The concentration of M71 (MVK + MACR), which is an oxidation product of isoprene, showed diurnal cycle similar to e.g. M33 and M59. The ratio of the concentration of M71 to that of M69 also behaved differently to that observed by Ammann *et al.* (2004). Instead of having a daytime minimum and nighttime maximum the ratio behaves in an opposite way. In a previous study at the Hyytiälä site, based on daily afternoon air samples, Hakola *et al.* (2003) suspected an anthropogenic source of MVK.

For calculation of the total monoterpene concentration M81, M82 and M137 were summed up. M82, having a very high factor loading on factor 2, and correlating well with M81 (r^2 = 0.97) is thus also assumed to be limonene fragment, even though the concentration of M82 is only about 6% of the concentration of M81. The time-series of the total monoterpene concentration is shown in Fig. 7, together with total monoterpene concentrations analyzed from adsorbent cartridges. The daytime total monoterpene concentrations varied between 200 and 500 ppt$_v$ and nighttime concentrations reached frequently 1 ppb$_v$ or more. However, the nighttime concentrations above canopy were much lower than the sub-canopy concentrations (Fig. 6). The speciation of the total monoterpene concentrations (Table 2) shows the most abundant mono-

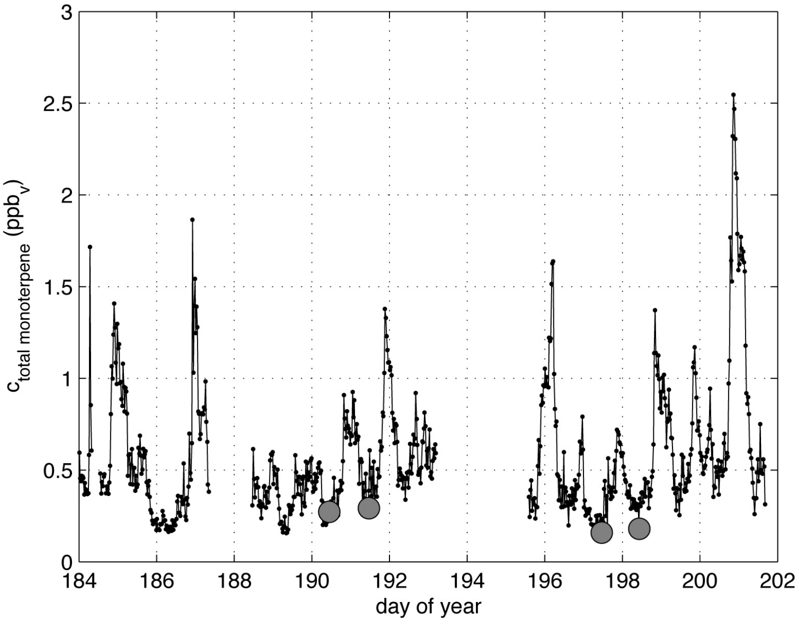

Fig. 7. Total monoterpene concentration measured by the PTR-MS as the sum of concentrations of M81, M82 and M137 (Line and small black dots), and total monoterpene concentration analyzed by GC-MS from adsorbent samples (large gray dots). The PTR-MS data are presented as half-an-hour averages and on the *x*-axis is the day of the year with tick marks at midnight. The adsorbent samples were collected for one hour.

terpenes to be α-pinene and Δ^3-carene. Also the total monoterpene concentrations obtained by the GC-MS analysis of the adsorbent samples, and simultaneous PTR-MS measurements are shown in Table 2. As the air was sampled onto the adsorbent cartridges above the forest canopy at 20 meters, and into the PTR-MS below the canopy at two meters, somewhat higher concentrations by PTR-MS are expected. The concentrations obtained by the two measurements are in the same range, and somewhat higher were as expected measured by the PTR-MS. However, the amount of the data from the GC-MS is very limited and only from the afternoon hours. Therefore future intercomparisons are needed.

Conclusions

On-line measurements of atmospheric concentrations of volatile organic compounds (VOC) by proton-transfer-reaction mass-spectrometry (PTR-MS) were conducted in a boreal forest ecosystem for two and a half weeks in the summer of 2004. Many of the compounds measured show strong diurnal variations in concentrations indicating local sources or sinks.

The masses measured were divided into three classes by factor analysis based on the behavior of their concentrations. The first class was correlated with the ambient air temperature and light, and included reactive compounds with local

Table 2. Concentrations of monoterpenes analyzed from adsorbent cartridges using GC-MS technique (ppt$_v$) and total monoterpene concentration measured by PTR-MS as sum of M81, M82 and M137.

	8 July 10:20–11:20	9 July 10:52–11:52	15 July 10:50–11:50	16 July 10:00–11:00
α-pinene	124	141	66	69
β-pinene	13	23	16	11
Δ^3-carene	110	99	55	55
Camphene	14	19	14	36
Sabinene	7	10	8	8
Limonene	0	0	0	0
Total MT	272	292	159	180
Total MT by PTR-MS	276	414	203	277

biological, anthropogenic or chemical sources. The compounds in this class, such as methanol, acetone, MVK + MACR, butanol and hexanal, had generally highest concentrations in late afternoons and minimums during nighttime. The class 2 included monoterpene masses and was correlated with the mixing time-scale having highest concentrations at night and lowest during daytime. The emissions of monoterpenes classified into this class are dependent only on temperature, whereas the sources of compounds in class 1 may be light dependent. Class 3 was not correlated with local meteorology and included rather long-lived compounds. Benzene, having strong positive loading, is emitted by anthropogenic activity.

The diurnal cycle of the concentration of M69, generally associated with isoprene, differed from those measured at mid-latitude sites with strong isoprene emitters by having maxima late in the evening. This might be due to the different light environment in the northern latitudes. The total monoterpene concentration measured by the PTR-MS and GC-MS were in the same range, even though the difference in the measurement height together with the limited amount of GC-MS data makes the comparison inconclusive. Therefore future intercomparisons are needed.

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