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Application of PTR-MS for measurements of biogenic VOC in a deciduous forest

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Abstract

The vegetation–atmosphere-exchange is an important process controlling the atmospheric concentration of various volatile organic compounds (VOCs) that play a major role in atmospheric chemistry. However, the quantification of VOC exchange on the ecosystem scale is still an analytical challenge. In the present study we tested and applied a proton-transfer-reaction mass spectrometry system (PTR-MS) for the measurement of biogenic VOCs in a mixed deciduous forest. VOC concentrations were calculated from the raw instrument signals based on physical principles. This method allows a consistent quantification also of compounds for which regular calibration with a gas standard is not available. It requires a regular and careful investigation of the mass-dependent ion detection characteristics of the PTR-MS, which otherwise could become a considerable error source. The PTR-MS method was tested in the laboratory for a range of oxygenated and non-oxygenated VOCs using a permeation source. The agreement was within 16% or better, which is well within the expected uncertainty.

During the field measurement campaign in a deciduous forest stand, an on-line intercomparison with a state-of-the-art gas-chromatography system showed a generally good agreement. However, the relatively low ambient VOC concentrations revealed some systematic difference for acetone and isoprene, that may indicate an error in the determination of the PTR-MS offset or an interference of an unidentified isobaric compound on the detected ion mass. With the presentation of selected field results, we demonstrate the ability of the PTR-MS system to measure continuous vertical concentration profiles of biogenic VOCs throughout a forest canopy at a time resolution of 20 min. The resulting datasets provide valuable information for the study of the interactions between emission, photochemical transformation and transport processes within and above the forest canopy.

Keywords: Proton-transfer-reaction mass spectrometry; PTR-MS; Volatile organic compounds; Biosphere–atmosphere exchange; Deciduous forest

1. Introduction

The vegetation–atmosphere-exchange is an important process controlling the atmospheric concentration of various volatile organic compounds (VOCs) that play a major role in atmospheric chemistry [1,2]. But there is still a lack of knowledge concerning the amount of reactive trace gases being emitted or deposited by forests and other ecosystems as well as the chemical processing of these compounds within the vegetation canopy.

The quantification of biogenic VOC exchange on the ecosystem scale is still an analytical challenge. Fast and sensitive systems are needed for simultaneous measurements of several substances at a high temporal resolution. Proton-transfer-reaction mass spectrometry (PTR-MS) [3,4] has the potential to fulfil these requirements. As a purely mass spectrometric method, PTR-MS has the intrinsic problem of uncertainty in the compound identification from mass information only. On the other hand, most of the relevant biogenic VOCs including oxygenated compounds can be detected at

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time resolutions in the order of minutes or even faster, which is not possible with common GC systems.

For measuring VOCs with PTR-MS, two different approaches are applied to get the concentration from the instrument's raw signals. An empirical direct calibration of the PTR-MS raw signals with a gas standard (cylinder gas standard or permeation source) results in an effective sensitivity of the instrument for a given compound [5–7]. This approach relies on the quality and temporal stability of the gas standard and the stability of the instruments sensitivity (between calibration events). In addition, the experimental sensitivity is valid for the calibrated gas compounds only and generally cannot be applied to other VOCs.

The second approach is the calculation of the concentration based on physical and chemical principles, originally promoted as an intrinsic advantage of the PTR-MS method [3,4]. It relies on (theoretical) knowledge about the ion–molecule reaction kinetics as well as on instrumental characteristics and operation parameters. Although this approach has been applied in various studies, uncertainties about the correct calculation procedure remain, e.g., concerning the choice of reaction rate constants or the correction for non-constant detector response.

In the present paper, we report about laboratory experiments and field application of a PTR-MS system for biogenic VOC measurements within the framework of the ECHO project (Emission and Chemical transformation of biogenic volatile Organic compounds, see http://www.fz-juelich.de/icg/icg-ii/ECHO/echo.ger.html). The concentrations of various oxygenated and non-oxygenated VOCs were determined from the raw PTR-MS signals by a physical calculation procedure. Some relevant instrumental parameters were investigated for their influence and uncertainty. The quality of the calculation procedure was tested using a laboratory permeation source. During the field measurement campaign in a deciduous forest stand, an on-line intercomparison with a state-of-the-art gas-chromatography system was performed over several weeks. The PTR-MS was used to investigate the vertical concentration profiles of biogenic VOCs throughout the forest canopy at a high temporal resolution. Selected results of the field campaign are presented for illustrating the applicability and specific advantages and problems of the PTR-MS method for the investigation of biogenic VOCs.

2. Experimental

2.1. PTR-MS methodology and instrumental characteristics

The PTR-MS method and the commercially available instrument (IONICON Analytik GmbH, Innsbruck, Austria) have been described in detail in numerous publications (e.g., [3,4,6,8]). Nevertheless, a short description of the methodology and instrument characteristics is given here, since the present paper includes specific investigations on methodological and instrumental problems.

2.1.1. Proton-transfer-reaction

Every mass spectrometry method requires the ionisation of the compounds of interest, in the present case the VOC molecules in the air. The PTR-MS belongs to the group of chemical ionisation mass spectrometers. The compounds of interest are not ionised directly by means of electrons or radiation, but the ionisation happens in a "soft" way through a proton-transfer from previously produced primary ions. The PTR-MS system uses hydronium ions H_3O^+ as primary ions. They are produced by a high voltage discharge in a hollow cathode flushed with pure water vapour. The H_3O^+ ions are accelerated into a drift tube continuously flushed with sample air. There the H_3O^+ reacts with any air constituent having a higher proton affinity than water vapour. Among the compounds commonly present in the atmosphere, such high proton affinities are found for many volatile organic compounds [4] with exception of the alkanes and small alkenes and alkynes. The main air constituents like N_2, O_2, CO_2, CO, CH_4, O_3, and nitrogen oxides exhibit a low proton affinity and do not react with H_3O^+. The hydronium ion is, therefore, most suitable for a selective reaction with VOC compounds in ambient air.

When colliding, the H_3O^+ ion easily transfers a proton to a VOC molecule:

$$H_3O^+ + \mathrm{VOC} \xrightarrow{k} H_2O + \mathrm{VOCH}^+ \quad (1)$$

If the supply of H_3O^+ ions is sufficiently high, their concentration in the drift tube is not significantly decreased by reaction (1) with VOC compounds at typical ambient concentrations [4,9]. Therefore, the reaction kinetics can be linearised and the VOC concentration of interest can be calculated from the ion concentration ratio of the protonated trace gas molecule and the primary ion as:

$$[\mathrm{VOC}] \approx \frac{1}{kt} \frac{[\mathrm{VOCH}^+]}{H_3O^+} \quad (2)$$

The parameter t represents the reaction time corresponding to the transit time of the primary ions through the drift tube. It is determined by the accelerating electrical field, the length of the drift tube, and the concentration of moderating molecules. For the present configuration of the instrument an average reaction time of 105 μs is specified. The reaction rate constant k for the ion–molecule reaction (1) can be calculated based on theoretical considerations. In the present study calculated capture rate constants k_c were used. For non-polar molecules, they were determined according to the Langevin theory [10], for polar molecules they are based on trajectory calculations by Su and Chesnavich [11]. Beside the molecular mass, the polarisability or the permanent dipole moment are the most important parameters influencing the rate constants of individual VOC compounds. The calculated k_c values for the compounds of interest for the present study

Table 1
Results of PTR-MS laboratory measurements with two permeation sources S1 and S2 each containing a mixture of VOC species (MVK: methylvinylketone; MACR: methacrolein)

Compound (with source number)	Source concentration (ppb)	Detected ion mass (amu)	Collisional rate constant k_c (308 K) (10^{-9} cm^3 s^{-1})	PTR-MS zero-air offset (ppb)	PTR-MS concentration (ppb)	PTR-MS recovery ratio (%)
Methanol (S2)	9.65 (±13%)	m33	2.69	2.78	8.88 (±4%)	92 (±14)
Acetaldehyde (S2)	18.96 (±9%)	m45	3.74	2.24	17.99 (±3%)	95 (±9)
Acetone (S2)	31.36 (±18%)	m59	3.94	0.66	31.78 (±3%)	101 (±18)
Isoprene (S1)	5.39 (–)	m69	1.99	0.07	5.60 (±3%)	104 (–)
MACR (S2)	19.41 (–)	m71	3.79	0.07	17.44 (±3%)	90 (–)
MVK (S1)	4.67 (±2%)	m71	(3.79)	0.07	3.92 (±4%)	84 (±4)
Benzene (S1)	1.24 (±2%)	m79	1.92	0.09	1.16 (±9%)	94 (±9)
Toluene (S1)	0.31 (±2%)	m93	2.17	0.06	0.36 (±25%)	114 (±25)
Mixed monoterpenes (S2)	3.42 (±16%)	m81, m137	(2.00)	0.11, 0.01	2.86 (±6%)	84 (±17)

Percentage values in parenthesis give relative errors derived from non-linearity of weight loss (source) or variability of ion count rates including offset measurements (PTR-MS). k_c values in parenthesis were not individually calculated for the respective compound. The monoterpene mixture contained β-pinene, 3-carene and limonene at similar fractions.

are listed in Table 1. They are in the range between 1.9 and 4.0×10^{-9} cm^3 s^{-1}.

The concentration quantities in Eq. (2) represent conditions in the reaction area (drift tube). For deriving the trace gas concentration under ambient conditions, the temperature and pressure in the drift tube has to be known. The latter was kept at a value of 2.00–2.05 mbar. Such a low pressure in the reaction area limits the sensitivity of the instrument (yielding some 10 counts per second (cps) per ppb), but it keeps the formation of $H_3O^+(H_2O)_n$ clusters low. This configuration is in contrast to atmospheric pressure chemical ionisation mass spectrometers (see e.g., [12]) that work at high pressure, and therefore, exhibit higher sensitivity, but have to deal with high and varying cluster fractions. The drift tube temperature was not controlled by a thermostat. It varied between 30 and 39 °C with changing temperature conditions in the laboratory and field container. Theoretical calculations were performed with an average temperature value of 308 K inducing an error in the concentration results below 3%.

2.1.2. Relating VOC compounds to detected masses

In the PTR-MS, primary ions and protonated VOC ions are passing a single quadrapole mass filter and are detected by a secondary electron multiplier (SEM). Ion hits are counted within integer amu (atomic mass unit) classes for a specified dwell time. In the following, the ion mass is given without unit, e.g., as mass 21 or m21, and the corresponding detector count rate as *i*(m21). The attribution of detected masses to VOC compounds is a crucial problem of the PTR-MS method. Firstly, ions with the same mass cannot be distinguished. Among biogenic VOCs, this limitation concerns, e.g., the oxidation products of isoprene, methylvinylketone (MVK) and methacrolein (MACR), that are both detected at mass 71, or the various monoterpenes (α-pinene, β-pinene, limonene, sabinene, 3-carene, etc.) that all have a protonated ion mass of 137. For these compounds, the measurement results are interpreted as a sum concentration of the respective compounds.

On the other hand, some product ions undergo collision induced fragmentation. The resulting fragment ions are detected at a different mass. The fragmentation usually occurs not completely but at a certain fraction depending on the *E*/*N* ratio (electric field/particle density) in the drift tube [4]. Since the electric field and the pressure in the drift tube are usually held constant, the fragmentation rate can also be assumed constant. Among the VOC species investigated in the present study only isoprene and the monoterpenes showed significant fragmentation effects. The normal product ion of isoprene is detected at mass 69. In laboratory experiments with sample gases of known composition, a fragment signal was observed at mass 41 showing a fairly constant fragmentation rate m41/m69 of 16% (±2%). This fixed ratio was used to correct the m69 signal in the field, where the m41 signal is expected to be less specific for isoprene and may include fragments of other (unknown) compounds. The normal product ion of the monoterpenes has mass 137. However, a considerable fragmentation to mass 81 is generally observed with ion ratios m81/m137 up to one or even higher. Tani et al. [13] also showed that different fragmentation rates are observed for the various monoterpene species. For these reasons, the fragment fraction cannot be assumed constant for field measurements. Therefore, we generally used the sum of masses 81 and 137 for calculating the total monoterpene concentration in the present study. In principle, the different fragmentation patterns of isobaric compounds can be used for their differentiation [4]. However, this procedure would require accurate individual calibration of the fragmentation patterns, and the uncertainty grows rapidly with more than two possible compounds.

Another important issue for the appropriate ion quantification is the natural isotope composition of VOCs. Of quantitative relevance in the present context is only the ^{13}C isotope, that accounts for about 1.1% of biogenic C-atoms. The total fraction of isotopic VOC molecules increases with the number *n* of C-atoms in the molecules, it approximately equals *n* times 1.1%. Thus, for monoterpenes (C-10) it amounts to about 11% (see also [13]), which is not negligible. Since the

natural isotope ratio is fairly constant, the heavy isotopes were not measured regularly but were accounted for by a correction factor as quantified above. However, when using artificial VOC samples (pure liquids, permeation tubes, commercial gas mixtures), the actual isotope composition has to be checked.

Another isotopic effect of importance for PTR-MS measurements is the $^{18}O/^{16}O$ ratio that shows a fairly constant value of 500 (depending on the water source). The isotope ratio is not quantitatively relevant for oxygenated VOCs but allows to quantify the H_3O^+ ions at mass 21 instead of mass 19. Since the count rate at m19 is much higher than for the other masses of interest, the burden on the SEM is unnecessarily high when a scan mode with constant dwell time at all masses is applied. Therefore, the H_3O^+ count rate i(m19) is often determined as $500 \times i$(m21). An additional argument to avoid the detection of H_3O^+ at mass 19 is the observation of a non-linearity of the SEM at very high count rates (see below Section 3.1).

2.1.3. Transmission correction

The ion concentrations in Eq. (2) represent values prevailing in the drift tube. Since only the ratio of primary and product ions is needed, it basically can be replaced by the respective ratio of ion count rates detected at the SEM. However, the actual mass spectrometric unit of the PTR-MS instrument shows a distinct mass-selectivity in the relation between drift tube ion concentration and SEM count rate. This effect is described by a mass dependent transmission efficiency $\tau(m_{\text{ion}})$:

$$\frac{[\text{VOCH}^+]}{[\text{H}_3\text{O}^+]} = \frac{i(m_{\text{VOCH}^+})/\tau(m_{\text{VOCH}^+})}{500 \times i(\text{m21})/\tau(\text{m21})} \quad (3)$$

The transmission is generally lower for low masses like m19 or m21. It may be influenced by mass-selective behaviour of the quadrupole, the lenses, and the ion deflector between the quadrupole and the SEM detector.

$$\tau_{\text{rel}}(m_{\text{ion}}) \equiv \frac{\tau(m_{\text{ion}})}{\tau(\text{m21})} \quad (4)$$

The relative transmission of a certain mass (compound) can be determined by sampling the respective compound at such a high concentration, that the primary ion signal decreases significantly. The ratio of the product ion increase and the primary ion decrease reflects the relative transmission (4). If this is done with several VOC compounds of different mass, one should be able to determine an overall mass-dependence function of the transmission. A common simple way to produce a high VOC concentration is to hold the headspace of a pure liquid VOC sample close to the PTR-MS inlet. This usually produces a short excess concentrations in the drift tube, so that all H_3O^+ ions are used up in producing the respective VOC ions, and the respective primary ion signal temporarily vanishes. However, this procedure was found to give results with considerable scatter not suitable for obtaining an accurate transmission value. We, therefore, prepared air samples with adjusted VOC concentrations in tedlar bags that provided a constant sampling concentration over several minutes and reduced the H_3O^+ signal by only 30–70% [9].

2.1.4. Determination of background signal

In addition to the sensitivity (span) effects discussed so far, considerable offset signals are observed in the PTR-MS for many ion masses. They may be caused by desorption of impurities inside the sampling system and the drift tube [9]. In order to minimise inner surface effects, all wetted parts of the inlet tubing, fittings, and valves consisted of PFA (perfluoroalkoxy), stainless steel, and Silcosteel®. The offset signal for the various masses is determined by applying VOC free zero-air to the instrument. In the present case, the VOCs were removed from the sample air by directing it through a catalytic converter that is supposed to completely oxidise all VOC compounds. The converter consists of a half-inch stainless steel tube of 15 cm length filled with Platinum wool (TC catalysis set, Shimadzu Switzerland GmbH) and heated to 450 °C. Typically high values of the zero-air signal, corresponding to concentrations of 0.5–3 ppb, were observed for the detected masses of the oxygenated compounds methanol (m33), acetone (m59) and acetaldehyde (m45). For the other compounds, much lower offset values below 150 ppt were found (see Tables 1 and 2). Yet, most offset concentration values are of the same order of magnitude as commonly observed ambient VOC concentrations. Therefore, an accurate offset quantification and correction was crucial for the quality

Table 2
Typical (median) ambient concentrations of various VOC species as observed by PTR-MS during the field campaign, and corresponding average values and variability of the zero-air offset signals (in ppb units)

Compound name	Detected ion mass (amu)	Typical ambient concentration (median) (ppb)	Average offset (zero-air) (ppb)	Overall offset variability (S.D.) (ppb)	Short-term offset variability (hour-to-hour) (ppb)
Methanol	m33	3.180	2.375	0.379 (16%)	0.090 (4%)
Acetaldehyde	m45	0.528	1.118	0.426 (38%)	0.038 (3%)
Acetone	m59	1.444	0.339	0.132 (39%)	0.021 (6%)
Isoprene	m69	0.178	0.144	0.104 (72%)	0.011 (8%)
MACR + MVK	m71	0.091	0.087	0.051 (58%)	0.006 (7%)
Benzene	m79	0.110	0.174	0.132 (76%)	0.014 (8%)
Toluene	m93	0.196	0.059	0.029 (49%)	0.008 (13%)
Monoterpenes	m81, m137	0.089	0.048	0.025 (51%)	0.009 (19%)

of the PTR-MS measurements. The offset values varied considerably with the temperature of the drift tube (30–39 °C, see above) which typically showed a diurnal cycle. Therefore, the offset was determined periodically, at least once every hour. The converter was flushed continuously with sample air at a rate of 500 ml min^{-1} and the zero-air was switched to the PTR-MS by a three way valve.

2.1.5. PTR-MS operation parameters

The original inlet flow controller of the PTR-MS instrument had been replaced by a pressure controller that maintained an inlet flow (bypass flow) of about 150 ml min^{-1}. From this bypass flow, an effective sample flow of about 20 ml min^{-1} branched off into the drift tube via a capillary flow restrictor. The pressure controller maintained a constant pressure in the drift tube of approximately 2 mbar. In combination with the voltage of 600 V applied to the drift tube over its length of 9.5 cm, this resulted in a *E*/*N* ratio of about 130 Td in the drift tube. This value corresponds to the standard configuration of the commercial PTR-MS instrument and is thus similar to most applications reported in the literature.

As mentioned above the possible formation of water clusters is kept low in the PTR-MS primarily by the high *E*/*N* ratio in the drift tube. In addition, the water vapour flow to the ion source and the humidity of the sample air have some influence on the cluster formation. In the present configuration of the PTR-MS instrument, the water vapour flow was set to 10 ml min^{-1} and the main $H_3O^+(H_2O)$ water cluster signal as detected by the SEM at mass 37 was always below 5% relative to the normal hydronium signal. The reaction of VOCs with cluster ions depends on the specific compound [14]. A quantitative correction of this effect for PTR-MS measurements is problematic due to the (unknown) de-clustering efficiency after the drift tube [6] and, therefore, was not performed here.

Another potentially interfering reaction in the drift tube is the reaction of VOCs with O_2^+ and NO^+ ions [15,16] produced from air molecules diffusing back into the hollow cathode. By adjusting the voltages between the source and the drift region as well as the water vapour flow, the concentration of these interfering ions was kept below 2% of H_3O^+.

2.2. Online GC-FID system

The custom-made on-line system used for sampling and measuring VOC concentrations is described in detail in Komenda et al. [17]. The system is fully automated and has a time resolution of ∼30 min. During a sampling interval of 5 min, air is pumped through a multi-layer adsorption tube containing a mixture of 50 mg Tenax TA (60/80 mesh, Macheray & Nagel) and 150 mg Carbopack X (20/40 mesh, Supelco). The temperature of the tube is kept constant at 30 °C and the sampling flow is adjusted by a mass flow controller at 100 ml min^{-1}.

It has been shown in several studies before, that the sampling of VOCs on solid adsorbents in ozone containing air leads to degradation of VOCs on the adsorbents, artefact formation and several other problems. In the field, ozone removal from ambient air samples was carried out by adding 1.1 ppm NO to the sample air stream. With a rate constant of 1.82×10^{-14} cm^3 s^{-1} (at $T = 298$ K) for the reaction $NO + O_3 \rightarrow NO_2 + O_2$ the lifetime of ozone is about 2 s which is sufficient to destroy all ozone before the air sample reaches the adsorbents.

For the analysis, the VOCs are thermally desorbed (Tekmar, Aerotrap 6000) into a cryo-focussing device (Fisons Instruments, Cryo 820) where they are pre-concentrated at −130 °C. Peak separation is then performed on a chromatographic column (Optima-5-MS, 30 m length, 0.25 mm i.d., 0.5 μm film). The initial temperature of the GC oven is held at 40 °C for 3 min and then ramped to 160 °C at a rate of 15 °C min^{-1}. Helium is used as carrier gas at a flow rate of 2.1 ml min^{-1} and VOCs are detected with an FID (Fisons Instruments, MD 800). Beside pure hydrocarbons, the system is able to detect some oxygenated VOCs, of which MVK, MACR, and acetone are of special interest for the comparison with PTR-MS. The sensitivity to the various compounds was calibrated using a custom-made diffusion source described in detail by Komenda et al. [18].

2.3. Laboratory experiments and standard gas mixtures

The performance of the PTR-MS system was tested for a range of VOC species during an inter-calibration experiment at the Research Centre Jülich in Mai 2002. Two permeation sources similar to the one described by Schuh et al. [19] were used to produce two complex mixture of VOCs with mixing ratios in the range between 0.3 and 32 ppb (Table 1). The sources contained some additional compounds that were not suitable for PTR-MS test measurements—due to unknown fragmentation or back-reaction effects or very low concentrations—and were, therefore, not included in the present study. Pure liquid samples of the various VOC species were contained in glass vials covered with Teflon membranes. The vials were placed in a temperature controlled (25 °C) permeation chamber that was continuously flushed with high purity nitrogen at a controlled flow rate. The VOCs permeating through the membranes were diluted in the nitrogen flow to concentrations of a few ppm. By use of a capillary restrictor flow split, a small fraction of the calibration gas was further diluted with synthetic air to concentrations of a few ppb. The synthetic air was humidified with high purity water to a dew point of 10 °C, controlled by the temperature of the humidifier. The mass loss rate for each VOC was determined regularly by weighing of the glass vials. The permeation rates were then calculated from the mean mass loss rate and the gas flow rates of the dilution steps.

In order to check the temporal stability of the PTR-MS performance, additional standard gas measurements were performed every few weeks including the beginning and the end of the field measurement campaign using a multi-component cylinder gas standard (National Physical Laboratory, Middlesex, UK) containing a mixture of alkanes, alkenes and

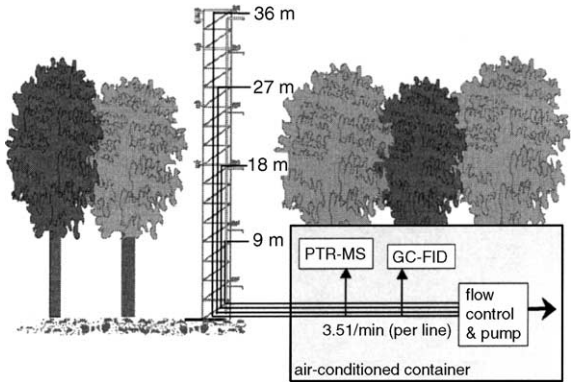

Fig. 1. Field setup for the VOC profile measurement by PTR-MS and GC-FID at the main tower in the Jülich forest.

alkynes (C2–C7) as well as aromatics all in the low ppb range. Of these compounds the PTR-MS is able to unambiguously measure isoprene (m69) and toluene (m93) as well as the sum of benzene, xylenes, and ethylbenzene (m79 + m107).

2.4. Field measurement site and setup

During the intensive ECHO field campaign between 1 June and 12 July 2002, the PTR-MS was operated at the base of a 36 m high tower ("main tower") in the mixed deciduous forest of the Jülich Research Centre, side-by-side to the online GC-FID system described above. Air was sampled through equally long tubes (50 m) from four inlets on the tower at 9, 18, 27 and 36 m above ground (see Fig. 1). Each inlet was equipped with a Teflon filter of 0.5 μm pore size. The height of the forest canopy was about 32 m. The direct surrounding of the main tower was dominated by an old beech stand with a leaf area index (LAI) of 5.7. The adjacent forest areas consisted of variable mixtures of oak, beech, and birch trees. The PFA sampling tubes (4 mm i.d.) were heated to about 60 °C to avoid condensation and wall sorption effects and flushed continuously at a rate of 3.5 l min^{-1}. Both gas analysing systems were switched alternatively to the four sample lines by PTFE solenoid valves. The total residence time of the air in the sampling system was about 15 s.

The measurement sequence of the PTR-MS was controlled by a script language program of the quadrupole unit. It switched between the profile levels every 5 min performing a full profile measurement in 20 min. Offset measurements were initiated every one or two hours. Typically up to 20 different masses were sampled sequentially. The dwell time of the detector on the important VOC related masses (see Table 1) was 5 s resulting in a measurement cycle interval of about 1 min. On every profile level, five to six full cycles were performed in a row. The first one was discarded to allow an inlet flushing after the valve switching, the others were averaged. For the full four-level profile measurements, this procedure yielded an effective integration time per mass and profile level of about 40 s distributed over one hour. In some periods, all mentioned schedule intervals were doubled. The on-line GC-FID was operated in a different time schedule. It performed an individual measurement every 30 min and thus performed a full profile cycle in two hours.

During the first period of the campaign (1–10 July) both systems were not measuring the full profile, the GC system sampled only the uppermost level, the PTR-MS the uppermost two levels. Gaps in the dataset occurred due to instrument or data acquisition failures and due to calibration procedures or occasional special measurement activities.

Beside the two VOC analysing systems described above, many other meteorological and air chemistry instruments were operated at various heights on the main tower as well as at additional locations (see, e.g., http://www.fz-juelich.de/icg/icg-ii/echo/measurements/). They are not the subject of this study and are, therefore, not described here.

3. Results and discussion

3.1. Quantification of ion detection response

As mentioned in Section 2.1, the calculation of trace gas concentrations from ion signals requires accurate information about the mass-selective response of the ion detection. Therefore, some experiments testing the mass selective effects of ion detection were performed in the laboratory one year after the field campaign, partly motivated by unexplained behaviour of the PTR-MS during the field measurements. Between the field campaign and these laboratory tests, the SEM detector had to be exchanged. The new SEM was in use for about 10 months at the time of the measurements described in the following and was operated at a slightly lower voltage than the previous one had been set to during the field experiment. However, it is assumed that the presented results are of general significance and apply as well to other instruments with similar operation parameters.

3.1.1. Mass dependent transmission efficiency

For calculating the correct ion concentration ratio in the drift tube, the respective count rates have to be corrected for the mass-dependent transmission of the detector (see Section 2.1). The results of the experimental transmission measurements using methanol (m33), acetaldehyde (m45), acetone (m59), isoprene (m69), toluene (m93), and xylene (m107) are plotted in Fig. 2. In order to get a continuous transmission function for all ion masses, a sigmoidal Boltzmann function of the form

$$\tau_{\mathrm{rel}}(m_{\mathrm{ion}}) = A\left(1 - \frac{A}{1 + \mathrm{e}^{(m-B)/C}}\right) \quad (5)$$

with empirical parameters A, B, C was fitted to the experimental transmission data. The value for isoprene was not included in the curve fit, because it was considered to be more uncertain than the other points due to fragmentation effects. Since the transmission experiments were performed with the hydronium isotopes at mass 21, function (4) is equal to one for

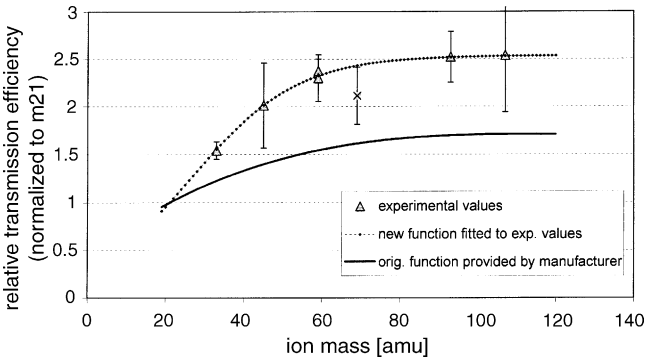

Fig. 2. Relative ion transmission efficiency between the PTR-MS drift tube and the detector as a function of mass. Symbols with error bars indicate the results of the transmission experiments to which a sigmoidal function (dashed line) was fitted. The symbol "×" denotes the discarded value for isoprene.

that mass and increases with higher masses until it reaches an almost constant maximum value above 80 amu. The fitted function differs systematically from the manufacturer's original transmission curve by more than 30% for higher masses. It is difficult to estimate an uncertainty of the experimental transmission curve. Whereas the results of the present experiment show a rather smooth course, this is not generally found in such experiments for other instruments as illustrated by Steinbacher et al. [9]. Considering the lack of theoretical basis for the shape of the curve and the observed temporal variability an uncertainty of 10–20% has to be expected especially for compounds for which no individual transmission was determined. The uncertainty might be even larger for masses above 120 amu.

3.1.2. Saturation effects at high count rates

According to the mass dependent transmission function in Fig. 2, one would expect a constant ratio of about 0.91 between the raw hydronium ion signal i(m19) and the respective value derived from the ^{18}O isotope as $500 \times i$(m21). Fig. 3 shows a comparison of the two quantities measured at varying ion source intensity (de-optimised by changing the source-drift voltage U3). For count rates up to about 6×10^5 cps, the agreement is very good, but at higher count rates the m19 signal deviates more and more from the 1:1 line. At 3×10^6 cps, the deviation is as large as 20%. The relation can be quantitatively described by a polynomial of second degree, i.e., it significantly deviates from a linear relationship expected solely due to the transmission characteristic.

This effect is comparable to observations with other SEM units (see Fig. 3) and other PTR-MS instruments. For lack of other explanations it may be attributed to a 'saturation' effect of the SEM detector at high count rates. In practice, it can be avoided by using m21 together with the known isotopic ratio instead of m19 for concentration calculations. In cases where m21 was not detected, we applied a relative correction to the m19 signal. The saturation effect also needs to be considered in transmission experiments (see following paragraph),

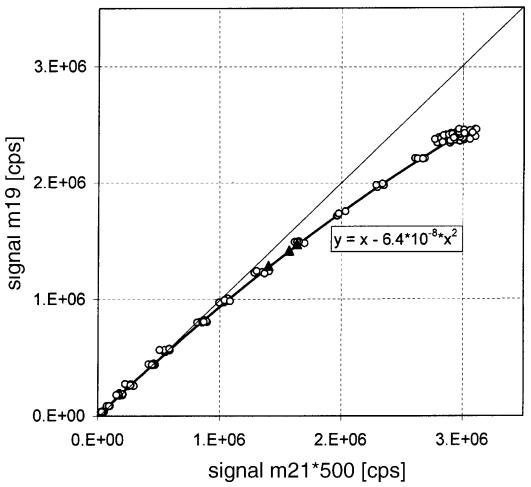

Fig. 3. Comparison of primary ion count rates i(m19) vs. $500 \times i$(m21) for varying ion source intensity; open circles: data obtained with new SEM by de-optimising procedure, triangles: data observed with old SEM during field measurement campaign, solid line curve: fitted polynomial function as given by numerical relationship.

where high count rates of protonated VOCs are produced. In that case the problem was avoided by de-optimising the primary ion source to count rates well below 10^6 cps.

3.1.3. Sensitivity dependence on SEM voltage

The SEM sensitivity depends on the applied voltage. By varying the voltage, a characteristic sensitivity curve as illustrated by the m21 signal in Fig. 4 is observed. According to the manufacturer, the voltage should be set to a value, at which the sensitivity starts to level off at the high end. If the voltage is set too high, the signal-to-noise ratio decreases and the aging of the SEM is accelerated. The aging process due to accumulated counts and oxidising effects shifts the SEM sensitivity curve to the right on the voltage axis, i.e., the applied voltage has to be increased to keep the same sensitivity. For a new SEM, the optimum voltage starts around 2500 V and

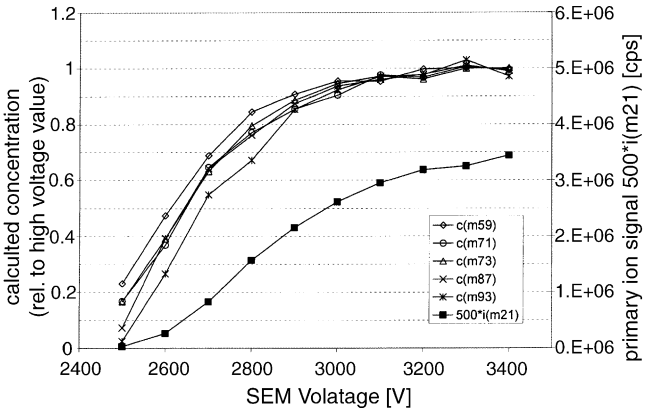

Fig. 4. Sensitivity dependence on SEM voltage: primary ion signal (right axis) and calculated concentrations for a constant sample gas mixture containing acetone (m59), MACR (m71), 2-butanone (m73), 2,3-butane-dione (m87), and toluene (m93) at concentrations in the low ppb range.

can be increased to a maximum of 3500 V (within a period of about one year).

In principle, the SEM sensitivity should not affect the PTR-MS concentration measurements systematically, because they only depend on the ion ratio and not on their absolute count rates. In order to examine the exact influence of SEM voltage on calculated concentrations, we performed a voltage variation experiment with fixed concentration of several VOC compounds provided by a controlled dilution of a custom-made gas standard (Apel & Riemer Environmental Inc., Denver CO, USA). The calculated concentrations are plotted in Fig. 4 in relative units. As the results demonstrate, a constant sensitivity only applies for the highest voltage range, 3200–3400 V in this case. For lower voltage values, the concentrations decrease similar to the primary ion signal. This means that the SEM response for higher masses decreases much faster with decreasing voltage than that for the m21 signal. As a consequence, the transmission characteristic as defined in (3) and (4) depends on the SEM voltage, if the latter is not within the optimum range. Since the levelling-off of the concentration signals at high voltages is more pronounced than for the primary ion signal alone, the concentration (essentially the ion signal ratio $i(m_{ion})/i(m21)$) is a better indicator for the choice of the appropriate SEM voltage.

3.2. Measurements of gas standards

3.2.1. Laboratory permeation source

The applicability of the PTR-MS with physical concentration calculation was tested in the laboratory with a VOC permeation source system. Table 1 shows a list of the measured VOC species with the gravimetrically determined source concentrations. They are compared to the results of the PTR-MS measurements obtained by physical calculation using the indicated k_c values.

The agreement of the calculated PTR-MS concentrations and the gravimetrically determined source concentrations is fairly good with maximum deviations of only 16%. The differences are mostly lower than the combined statistical uncertainties of the PTR-MS and the source concentrations. The biggest deviation is found for toluene, MVK, and the monoterpenes. In the first case, the uncertainty is due to the low concentration leading to a high relative variability of the PTR-MS results (including the offset error). In the other cases the difference may be attributed to errors in the reaction constants, that could not be determined individually. For MVK the value of MACR was adopted, and for the monoterpenes the standard value of 2×10^{-9} cm^3 s^{-1} was taken. Recently, Tani et al. [13] reported individual k_c values for α-pinene and limonene of 2.54 and 3.06 ($\times 10^{-9}$ cm^3 s^{-1}) respectively. These higher reaction constants, if valid also for the other monoterpenes, would lead to lower PTR-MS results and thus a significantly larger difference to the source values.

Sprung et al. [12] as well as Knighton and Grimsrud [20] give a significantly lower reaction rate constant k_c than used here for acetone of only 2.3×10^{-9} cm^3 s^{-1}. Such a value is obtained by the Su and Chesnavich parameterisation [11], if the so-called effective temperature including translational kinetic energy in the electrical field [21] rather than the normal temperature is used. However, as pointed out by Lindinger [10], fast ion–molecule reactions close to the collisional limit generally do not show a dependence on the kinetic energy of the reactants. Anyway, the lower k_c value would result in a very poor agreement for acetone in the present experiment.

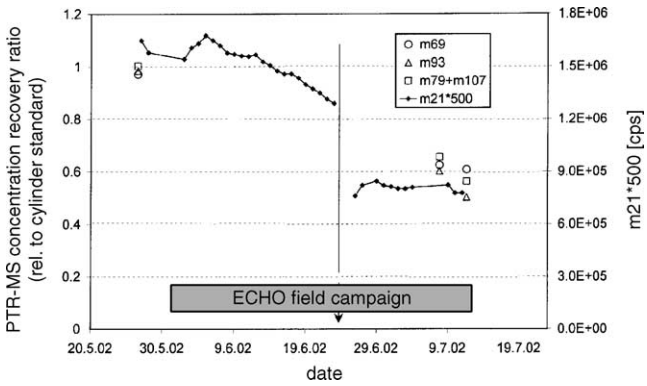

Fig. 5. Relative recovery rates of PTR-MS gas standard measurements (NPL cylinder gas standard) at the beginning and at the end of the field measurement campaign (squares, triangles, circles), and time series of H_3O^+ signal (solid line with diamonds) for a constant SEM voltage of 3300 V; arrow indicates date of dislocation of instrument.

3.2.2. Field comparison with cylinder gas standard

In order to check the temporal stability of the PTR-MS performance during the field experiment, a cylinder gas standard (see Section 2.3) was measured in the start and end phase of the campaign. The results are displayed in Fig. 5 as recovery ratios relative to the nominal values of the cylinder standard. Between the beginning and the end of the ECHO field campaign, the apparent sensitivity of the PTR-MS decreased by about 40%, almost equally for all compounds. Since the SEM detector of the instrument was already one and a half years old at the time of the field campaign and was operated at a constant voltage of 3300 V, the sensitivity drift has likely been caused by a shift of the SEM response curve as a consequence of the venting of the vacuum section for transports within the campaign in combination with the mass dependent sensitivity illustrated in Fig. 4.

Since mainly one significant drop in the H_3O^+ signal was observed in the middle of the measurement campaign (after a dislocation of the PTR-MS instrument), we assume that the general sensitivity drop was associated with that event, and therefore, we corrected the data of the second part of the campaign according to the drop in the cylinder standard measurements. Hence, these results were not derived purely by physical calculation but include a general empirical correction factor for the SEM sensitivity drift (same effect for all masses).

3.3. Field comparison with GC-FID

In contrast to the gas standard measurements presented above, field applications of PTR-MS always have an intrinsic identification problem due to potential mass interference of unidentified compounds in ambient air. In order to verify the mass–compound relation found with the standard gas mixture in the laboratory and to test the stability of the calculated PTR-MS results we compared them to the simultaneous GC-FID measurements. A comparison was possible for the following compounds that were successfully detected by both systems: isoprene, acetone, MVK + MACR, and benzene. The latter is not a biogenic compound but was included in the comparison for additional information about the general performance and comparability of the two systems.

The comparison of the PTR-MS and the GC-FID results in Fig. 6 show a generally good agreement in the temporal variations of the VOC concentrations. This indicates, that the main part of the detected MS signals can be attributed to the respective VOC species. However, there is a considerable scatter of individual data points due to the generally short and non-synchronous sampling time (noise effects and de-

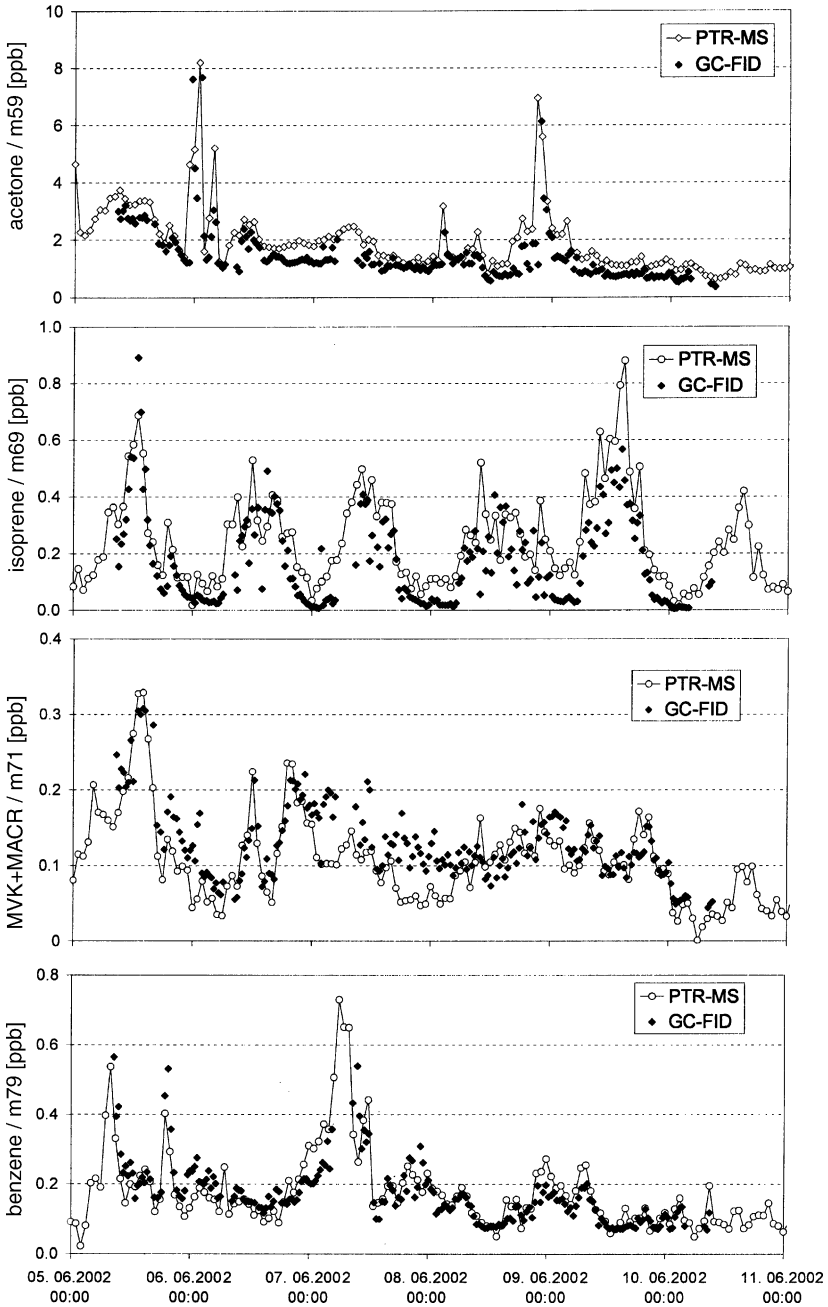

Fig. 6. Simultaneous measurements of various VOC concentrations above the forest canopy (36 m above ground) by PTR-MS and online GC-FID. PTR-MS data represent hourly averages, GC data are individual half-hourly measurements.

tection of different short term fluctuation states). For the sum of MVK and MACR as well as for benzene, no systematic deviation was found. Temporal variations in the agreement for MVK + MACR may be due to varying contributions and a different sensitivity of the instruments to the two compounds. The ratio of MVK and MACR as determined by the GC system was typically around 0.5 showing a general dominance of MACR but with a large variability of individual values.

For acetone and isoprene, a systematic difference is observed. Especially the distinct night-time difference of about 50 ppt in the case of isoprene suggests an offset or background effect rather than a (proportional) sensitivity error. Such effects are much more problematic for the PTR-MS than for the GC-FID system. Firstly, a systematic overestimation in the PTR-MS results can be caused by the interference of unexpected or unknown compounds on the detected ion mass (e.g., a contribution of propion-aldehyde on m59). Secondly, the zero-air signals of the PTR-MS determined empirically by the catalytic converter are relatively high and well in the order of typical ambient air concentrations observed in the field (see Table 2). In addition, their origin is not well explained up to now and they show considerable variability. Considering the reduction between the overall and the hour-to-hour offset variability as indicated in Table 2, an hourly offset determination appears to be a reasonable practice. Yet it still leaves a significant uncertainty that might affect the measurement of low concentrations in particular. In contrast, for the comparatively high concentrations provided by the permeation source in the laboratory experiment (see Table 1) a conspicuous effect was not to be expected.

For compounds that undergo considerable fragmentation in PTR-MS measurements, potential interferences on one of the detected masses can be checked even without comparison to an independent method. For the detection of the monoterpenes, the sum of the masses m137 and m81 is used. It is assumed that the signal on m81 represents the sole relevant fragment of the monoterpenes and that it is unique, i.e., there is no interference by other compounds. The latter assumption can be tested by comparing the signals of m81 and m137 for individual measurements.

Such a comparison is displayed in Fig. 7. The high correlation coefficient indicates a fairly linear relationship between both signals, which were individually corrected for measured zero-air offsets. The span of the regression relationship indicates a high fragment ratio m81/m137 of about 5:3. The regression analysis also yields a small offset of 0.59 cps (corresponding to a concentration of 17 ppt) that is hardly statistically significant though. It is concluded that there is no clear evidence for a relevant interference of an unknown compound on one of the two detected masses.

3.4. Selected time series of hydrocarbons and oxygenated compounds

The following two sections present some selected results of the PTR-MS field measurements in order to demonstrate the potential and specific advantages of the PTR-MS method for the investigation of biogenic VOCs and the corresponding canopy exchange processes.

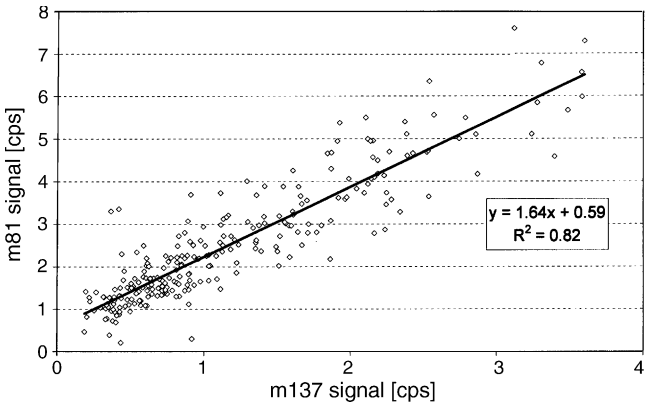

Fig. 7. Comparison of m81 and m137 mass signals detected by PTR-MS for ambient air measurements during the field campaign (zero-air values are subtracted). Solid line represents linear regression with displayed numerical relationship and regression coefficient.

A distinct advantage of the PTR-MS instrument in the field of biogenic VOC research is the ability to detect most relevant non-oxygenated as well as the oxygenated compounds. This is generally problematic for GC systems, especially the quantification of methanol and aldehydes requires specific designs and configurations of GC systems that are often unfavourable for the detection of other compounds. Fig. 8 shows a 6-day period of concentration time series of biogenic hydrocarbons and oxygenated compounds measured on the tower top above the forest canopy. Within the forest stand around the measurement site, monoterpenes are emitted by birch and beech trees whereas the third important species, the oak trees, are known as isoprene emitters.

Because of their relatively short lifetime in the atmosphere (in the order of 1 h), the directly emitted hydrocarbons like isoprene and monoterpenes show a concentration pattern that follows the respective emission pattern, which is controlled by the diurnal course of light and temperature [19,22]. This behaviour is also illustrated by the mean diurnal cycles of isoprene and global radiation in Fig. 9. The concentration starts to rise shortly after sunrise, reaches a maximum value in the afternoon and drops rapidly after sunset.

The concentrations of the oxygenated compounds displayed in Fig. 8 (methanol, acetone, acetaldehyde, MVK + MCR) follow the day-to-day trend of isoprene and monoterpenes, but they don't show a pronounced diurnal variation. This can be explained by the comparably longer lifetime of oxygenated compounds (few hours to days, see e.g., [23–25]) leading to only minor concentration decays during the night and an overall accumulative behaviour relative to the reactive precursors like isoprene and monoterpenes. This behaviour is illustrated by the mean diurnal course of the main isoprene oxidation products (MVK + MACR) in Fig. 9.

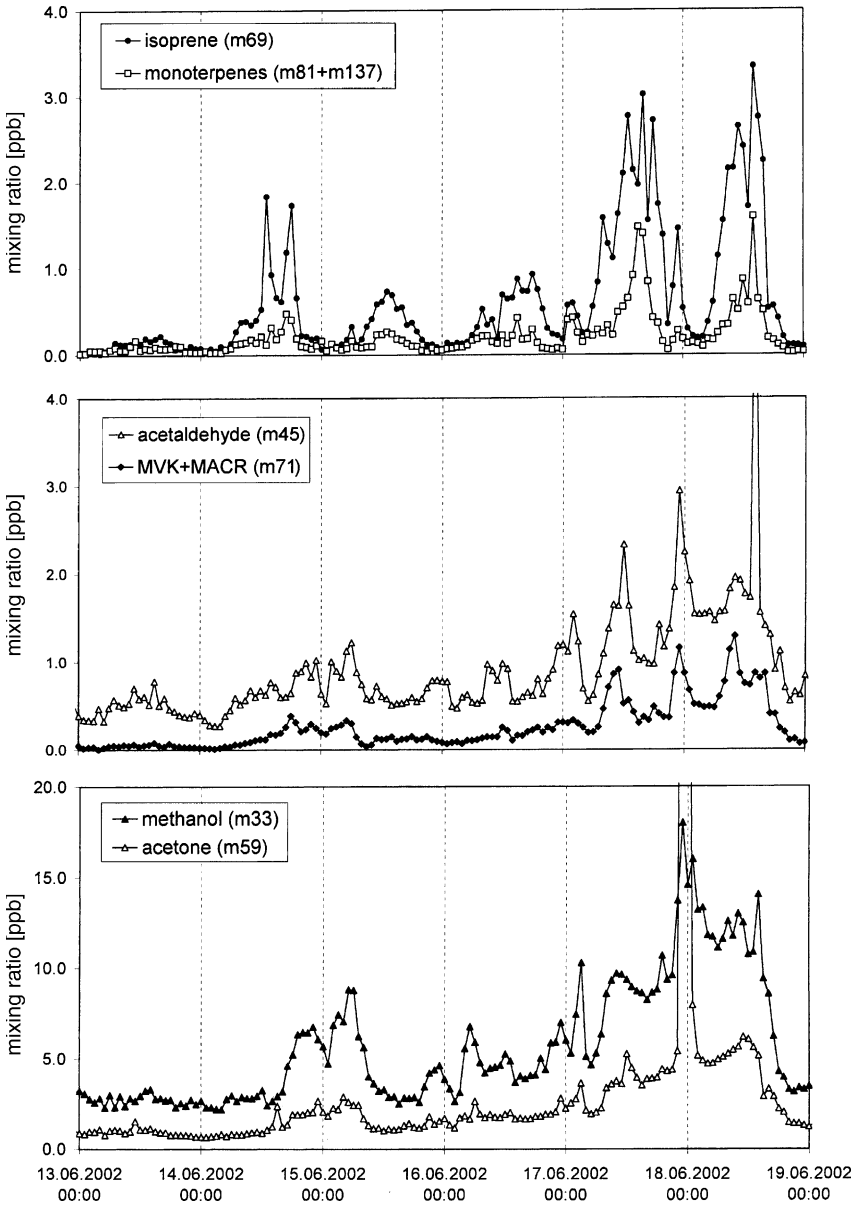

Fig. 8. Ambient concentration time series of non-oxygenated (upper panel) and oxygenated (middle and lower panel) biogenic VOCs, measured by PTR-MS above the forest at 36 m above ground.

Because of their longer lifetime, the concentrations of oxygenated compounds observed at a specific site are less dependent on local biogenic emissions but much more on variations of the air mass advection (i.e., changes in wind direction and synoptic weather conditions). For instance, the distinct concentration drop of all oxygenated compounds in Fig. 8 in the evening of 18 June was associated with the passage of a strong cold front marking the advection of a new and relatively clean air mass.

Under some idealised assumptions, concentration ratios of directly emitted VOCs and their photochemical oxidation products in the atmosphere can be used to characterise the photochemical age of an air mass [23]. Fig. 9 shows the diurnal variation of the concentration ratio (MVK + MACR)/isoprene as quantified by PTR-MS. During daytime, the ratio is fairly constant with mean values of about 0.3. These results are higher than published values measured over forest by Apel et al. [26] (approximately 0.1), but they are more comparable to results of Montzka et al. [27] (0.35–0.5) and indicate a considerable contribution of oxygenated compounds advected by aged air masses. The potential interference effect on mass 69 (see Section 3.3) would have only a minor effect on the above-discussed ratio during daytime when isoprene concentrations are high, but it strongly raises the relative uncertainty of the night-time results making them hardly significant.

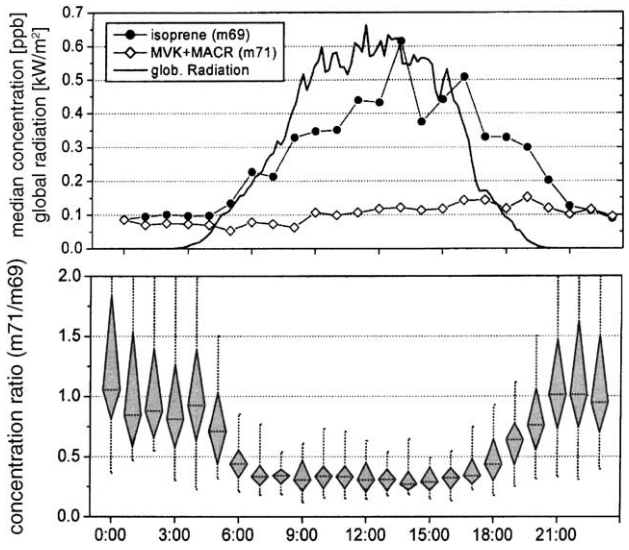

Fig. 9. Upper panel: mean diurnal cycles of isoprene (m69) and its oxidation products MVK + MACR (m71) measured by PTR-MS, and mean global radiation for the entire measurement campaign. Lower panel: diurnal variation of ratio [MVK + MACR]/isoprene (m71/m69) measured by PTR-MS, diamond boxes indicate median (middle horizontal line), quartiles (cone ends of boxes) as well as the 10 and 90% quantiles (ends of whiskers).

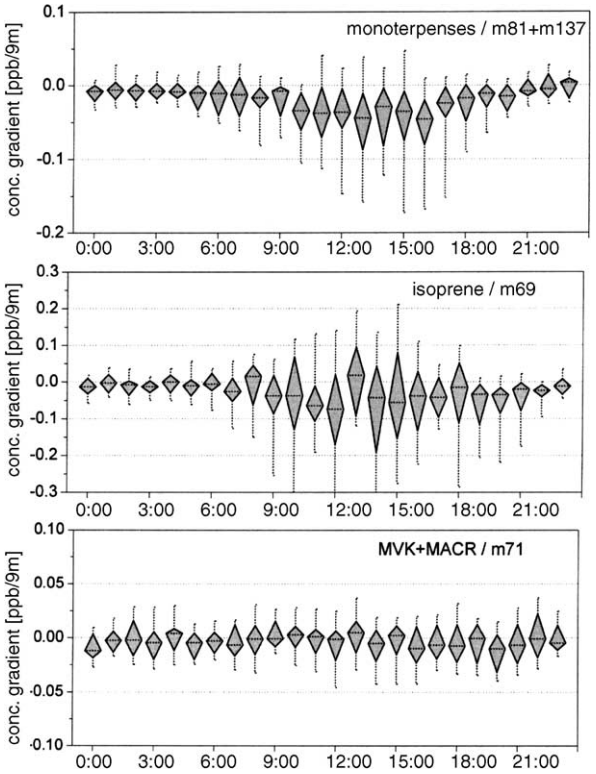

Fig. 10. Diurnal variations of hourly mean concentration gradients between the uppermost two measurement heights (36 and 27 m) for various VOCs. Day-to-day variability of individual measurements over the entire field campaign is characterised by diamond box-plots (description see Fig. 9).

3.5. Concentration gradients and canopy profiles

The variations of biogenic VOC concentrations with time and with height in the forest contain information about their biological and photochemical sources and sinks, as well as the influence of exchange processes between the canopy and the atmosphere. Beside the direct interpretation of VOC profile data (together with other chemical and meteorological measurements), they are also valuable for the validation of novel canopy models that combine chemistry with radiation and transport processes.

3.5.1. Vertical gradients at canopy top

Vertical concentration gradients at the top of the forest canopy give a semi-quantitative information about the net forest-atmosphere transfer of the respective VOC compound. During daytime, the efficient turbulent mixing between the canopy layer and the air above results in relatively small mean concentration gradients but considerable short term concentration variability for locally emitted compounds. As a consequence, precise and representative concentration measurements on different heights are necessary to resolve gradients over typical averaging intervals of 30–60 min.

In Fig. 10, vertical concentration gradients (difference between the two uppermost measurement levels) are displayed as box-plots. The indicated scatter range is a product of day-to-day variability (due to changing weather conditions) as well as of statistical measurement uncertainty. Only for monoterpenes, an overall systematic diurnal cycle in the vertical gradient is observed, with typical median values of about −30 ppt/9 m. It indicates a general emission of monoterpenes from the beech dominated forest around the measurement tower. For isoprene, mean gradients are also predominantly negative during daytime, but the individual data exhibit a large variability and thus a less consistent picture than for the monoterpenes. This may be explained by the less uniform distribution of the isoprene emitting oak trees growing especially north and west of the main tower and in more distant parts of the forest. The gradients of the oxygenated compounds detected on mass 71 are generally close to zero and thus show no indication of a net emission or deposition from/to the forest. This is not astonishing because they are not emitted directly from the vegetation but produced through photochemical oxidation in the atmosphere. Assuming a general zero-gradient for m71, the data in Fig. 10 give an estimate of the effective resolution (or detection limit) of the PTR-MS measurements. In the majority of the cases, the measured concentration difference was less than 25 ppt given a mean concentration of about 100 ppt (see Fig. 9).

3.5.2. Mean canopy distribution of monoterpenes

Considering the variability of the gradient data displayed in Fig. 10, a comprehensive and illustrative display of 30 days of full profile data is generally difficult. In the case of monoterpenes showing a fairly systematic behaviour, an averaging procedure seems to be meaningful. The temporal and spatial information of the profile time series are visualised in

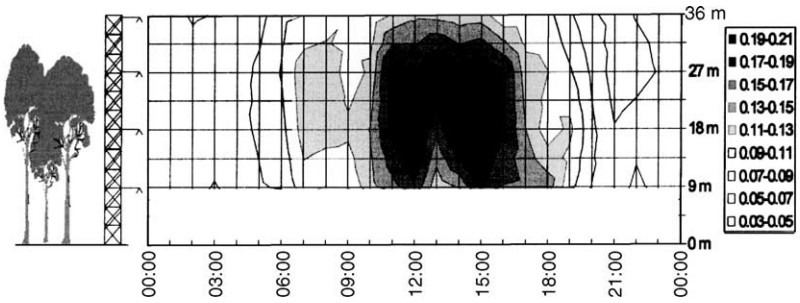

Fig. 11. Contour plot of mean monoterpenes concentration vs. time of day and height above ground. Data are median values over 30 days. Concentration values are indicated by the grey scale with steps of 0.02 ppb (see legend).

Fig. 11 as a contour plot of mean concentration versus time of day and height above ground. It shows a distinct concentration maximum during daytime in the crown region (14–28 m above ground) of the forest canopy, where the main emission by sunlit leaves takes place.

For isoprene, the mean distribution over 30 days gives no consistent picture and, is therefore, not useful for analysis and interpretation of the profile measurements. Therefore, data of individual days have to be analysed separately. The contour plot in Fig. 12 displays the development of the vertical isoprene distribution on 17 June, a clear and hot summer day. Beside the pronounced diurnal cycle of the isoprene concentration (also shown in Fig. 8), a distinct structure in the vertical profile can be observed. Around midday, the highest concentrations are found above the forest reaching down into the upper crown region. Below, the concentration is significantly lower. This pattern indicates a dominant advection of isoprene emitted further upwind and no major local isoprene source in that wind direction.

In the evening, a pronounced change in the concentration distribution occurs, resulting in maximum values within the canopy. A look at the meteorological measurements on this day (Fig. 12, upper panel) shows almost clear sky conditions illustrated by the regular diurnal radiation cycle. However, a pronounced shift of the wind from eastern to northern directions is observed in the afternoon. It coincides with the downshift of the concentration maximum to within the canopy. These results indicate the advection of isoprene from some distant sources in easterly direction before 16:00 and afterwards the effect of near isoprene emitting trees from the north. Qualitatively, this is in agreement with information from vegetation maps of this forest. While the area east of the tower is dominated by beeches (known as predominant monoterpenes emitters), the neighbouring area in the north has a higher proportion of oaks, which are strong isoprene emitters.

The presented results illustrate that the detection of diurnal variations of the VOC concentration profiles require a high time resolution of full profile measurements in the order of 1 h or less. Near-simultaneous sampling by frequent switching between the height levels is needed in order to avoid the interference of temporal variations in the vertical profile. Whereas a sufficiently high temporal resolution is usually not achieved by GC-systems, our results demonstrate that the

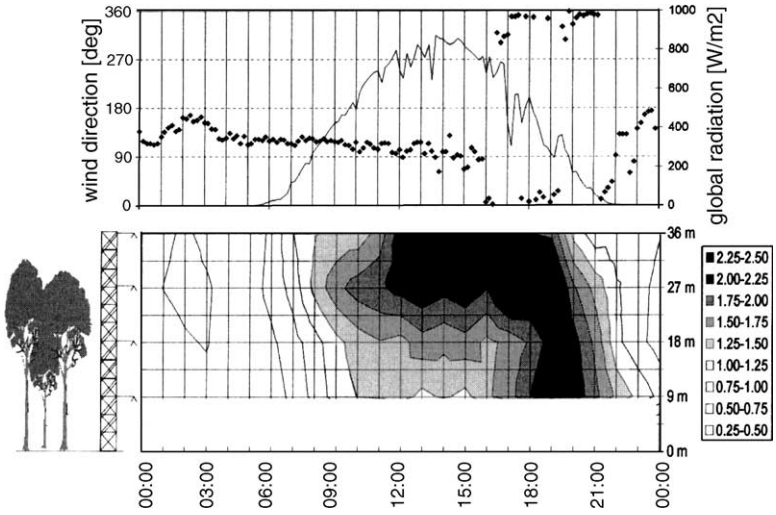

Fig. 12. Upper panel: wind direction (diamonds) and global radiation (solid line) measured at 37 m above ground about 200 m west of the main measurement tower; Lower panel: Contour plot of isoprene concentration vs. time of day and height above ground for 17 June 2002. Concentration values are indicated by the grey scale with steps of 0.25 ppb (see legend).

PTR-MS is able to perform such measurements continuously over several weeks.

4. Conclusions

In the present study we tested and applied a PTR-MS system for the measurement of biogenic VOCs in a mixed deciduous forest. VOC concentrations were calculated from the raw instrument signals based on physical principles. The calculation procedure allows a consistent quantification also of compounds for which regular calibration with a gas standard of sufficient quality is not available. However, it was shown that some specific detection characteristics of the PTR-MS instrument like the mass specific transmission, the saturation effect for large count rates, and the voltage dependent SEM sensitivity have to be investigated in detail.

A considerable uncertainty in the order of 10–20% has to be attributed to the transmission function, that was not determined directly at the time of the field measurements. The comparison with the original transmission characteristic provided by the manufacturer indicates that major quantitative shifts are possible. Additional uncertainty arises from the variability of individual transmission measurements and the lack of theoretical background for the shape of the mass-dependent function. It is presently not sure, whether it is supposed to stay constant for higher masses (above 100 amu) or to decrease again as, e.g., suggested by Steinbacher et al. [9]. An accurate determination method for the transmission characteristic is essential for the calculation method but also for the interpretation of sensitivity variations.

The uncertainty associated with the reaction rate k depends on the information and experimental results available for individual compounds. Comparison of theoretical calculations with experimental values [4,14] indicate a good accuracy of approximately 10% for many of the compounds investigated here. For VOCs with no individual k value available (MVK and monoterpenes) the uncertainty is estimated to be larger, in the order of 30%. The PTR-MS method was tested in the laboratory for a range of biogenic VOCs using a permeation source. The agreement was within 16% or better, which is well within the expected uncertainty due to the error sources mentioned above. It confirmed the validity of the collision rate constants calculated without the effect of translational kinetic energy.

Most of the discussed uncertainty sources relevant for physical concentration calculation may also become important for a direct calibration of the PTR-MS instrument with gas standards, if they vary with time between calibration events or if they are different for calibrations and ambient air measurements.

The comparison of simultaneous PTR-MS and GC-FID field measurements at a deciduous forest site showed a generally good agreement. However, the relatively low ambient VOC concentrations (comparable to the PTR-MS zero-air signal) revealed some systematic difference for acetone and isoprene, that may indicate either an error in the determination of the PTR-MS offset or an interference of an unidentified isobaric compound on the detected ion mass.

The relatively high background signal on some ion masses is a general problem of the PTR-MS instrument when measuring in the sub-ppb-range, because it shows considerable variability and its origin is not fully understood yet. Some improvement may be achieved in the future by a temperature control of the inlet system and drift tube, as well as the replacement of the Viton gaskets between the drift tube elements by Teflon parts (see [9,28]).

With the presentation of selected field results, we demonstrated the ability of the PTR-MS system to measure continuous concentration profiles of various oxygenated and non-oxygenated VOCs throughout a forest canopy at a time resolution of 20 min. The resulting datasets provide valuable information for the study of the interactions between emission, photochemical transformation and transport processes within and above the forest canopy. Possible improvements of the present setup include a faster switching between the measurement heights combined with a limitation to fewer masses, that will result in more precise high-resolution profile information, or an application for direct flux measurements [29,30].

Based on the present findings it can be concluded that the PTR-MS method with physically based concentration calculation yields satisfactory results for a range of biogenic VOCs. However, it is advisable to perform frequent checks with a reference gas standard to detect sensitivity drift effects and to determine the transmission function and the SEM voltage dependency regularly.

As already pointed out by Lindinger et al. [4], in a given environmental situation the probability of occurrence of isobaric compounds is often strongly reduced and thus facilitates the mass–compound-identification for PTR-MS measurements. Nevertheless, this is an intrinsic problem of PTR-MS applications in ambient air that makes the combined operation of a GC system very valuable as shown in the present study. While the PTR-MS provides the high time resolution necessary for special profile and flux investigations, the GC methods yields independent confirmation and information for detailed compound identification. Beside a parallel operation of independent PTR-MS and GC systems, also the combined GC-PTR-MS system proposed by de Gouw et al. [8] may represent a convenient solution.

Acknowledgements

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