A relaxed-eddy-accumulation method for the measurement of isoprenoid canopy-fluxes using an online gas-chromatographic technique and PTR-MS simultaneously

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Abstract

A relaxed-eddy-accumulation set-up using an online gas-chromatographic technique and proton-transfer-reaction mass spectrometry was applied to determine isoprenoid fluxes above a Norway spruce forest in July 2001/2002. The system was quality assured and its suitability for determination of canopy fluxes of isoprenoids was demonstrated. Flux measurements of oxygenated hydrocarbons failed the data quality check due to artefacts presumably arising from line and ozone-scrubber effects. Observations of turbulent fluxes of isoprenoids during the two field experiments show good agreements with primary flux data derived from enclosure measurements and modelling results using a canopy-chemistry emission model (CACHE). For monoterpenes maximum daytime fluxes of more than 2 nmol m\textsuperscript{-2} s\textsuperscript{-1} were observed, isoprene fluxes reached 1–1.5 nmol m\textsuperscript{-2} s\textsuperscript{-1}.

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1. Introduction

Reactive volatile organic compounds (VOC) play an important role in physical and chemical pro- cesses in the troposphere. In reactions involving O\textsubscript{3}, HO- and NO\textsubscript{3}-radicals, VOC cause substantial formation of secondary species such as O\textsubscript{3}, peroxyacyl nitrates (PANs) and other trace gases (Atkinson, 2000; Jenkin and Clemitshaw, 2000; Poisson et al., 2000; Wang and Shallcross, 2000). Additionally, the oxidation of some VOCs leads to the formation of condensable gases and eventually of atmospheric particles (Hoffmann et al., 1997;
Griffin et al., 1999; Matsunaga et al., 2003) which again will impact atmospheric chemistry, enhance cloud formation, and modify the Earth’s radiation budget (Brasseur et al., 1999).

The global anthropogenic VOC flux is estimated as $1 \times 10^{14} \text{g Ca}^{-1}$, while biogenic sources may be higher by one order of magnitude ($1.2 \times 10^{15} \text{g Ca}^{-1}$) (Steinbrecher, 1994; Guenther et al., 1995). Biogenic volatile organic compounds (BVOC) contribute significantly to the regional and global atmospheric photo-oxidant budget (Trainer et al., 1987; Biesenthal et al., 1998; Derwent et al., 1998).

Only detailed NO$_x$–VOC chemistry schemes (e.g. Derwent et al., 2001, 2005) in combination with good estimates of the initial conditions are able to describe ozone formation. Above-canopy flux studies on BVOCs such as isoprene and higher terpenes showed that net emissions from woody areas can differ significantly from primary BVOC emissions based on the sum of surface and canopy emissions. This is due to the high reactivity of such BVOCs, leading to a rapid decay within the forest stand (Ciccioli et al., 1999; Makar et al., 1999). Differences can be expected particularly pronounced on warm and sunny days with enhanced primary BVOC emission and photochemistry. There still exist substantial uncertainties about biogenic source strengths (e.g. Guenther et al., 1995; Simpson et al., 1999) and ignoring in-canopy chemistry may contribute to uncertainties of global BVOC sources. Adequate up-scaling methods and proper experimental determination of the net BVOC emission are therefore still needed (Fuentes et al., 2000).

Micrometeorological methods for net flux measurements allow the quantification of surface–atmosphere exchange of trace gases, including biosphere–atmosphere interactions. These methods are essential in developing and verifying up-scaling models. Eddy covariance (EC) is the most direct method. EC requires, however, data acquisition at high sampling rates of both wind velocity and trace gas concentration. Very few sensors exist for monitoring fast fluctuations of organic trace gases applicable in field flux experiments, e.g. a chemiluminescence system for isoprene (Guenther and Hills, 1998) and a tandem mass spectrometer for acetone and formic acid (Shaw et al., 1998). Karl et al. (2001) have demonstrated the capability of proton-transfer-reaction–mass spectrometry (PTR–MS) for EC measurements for a wider range of chemical species, however, the suite of compounds measured at a time is very limited (Karl et al., 2002). Methods derived from EC that allow VOC determination at lower rates either use subsets of full 10 Hz time series acquired by intermittent sampling, e.g. through disjunct eddy sampling (Rinne et al., 2001) or virtual disjunct EC (Karl et al., 2002), or sample air parcels separately for up-draughts and down-draughts (conditional sampling). Conditional sampling combined with continuous run-time analysis of the air flows in the up-draught and down-draught line was applied for CH$_4$ and N$_2$O flux measurements (). For nonmethane hydrocarbons (NMHC) accumulation procedures are commonly used, e.g. relaxed-eddy-accumulation (REA) as outlined by Businger and Oncley (1990).

Briefly, in REA applications air samples are drawn into two different reservoirs depending on the direction of the vertical wind $w$ (“up-draught” reservoir in case of $w>0$, “down-draught” reservoir in case $w<0$). After a period of 30 min the samples are analysed for $c^+$ and $c^-$ (accumulated concentration of a compound in the up-draught and down-draught pathway, respectively) by slow gas analysers. The flux is proportional to the difference of both terms $c^+$ and $c^-$. The relaxation process in the REA technique allows flows into both reservoirs, which are independent of the absolute value of the vertical wind speed $|w|$. Businger and Oncley (1990) showed that in this case the vertical flux depends on the concentration difference $c^+ - c^-$, the standard deviation of the vertical wind speed $\sigma_w$ and the dimensionless Businger Oncley parameter $b$ which depends on the atmospheric stability. This latter dependence is minimised by applying a threshold $|w_0|, i.e. the “up”-sample is collected in the case $w > w_0$, and the “down”-sample is taken in the case $w < -w_0$ (in the case where $-w_0 < w \leq w_0$, i.e. the “dead-band”, samplings are discarded). However, in this case $b$ becomes dependent on the width of the dead-band. The application of dynamic dead-bands (e.g. Christensen et al., 2000) where the threshold $|w_0|$ is a function of $\sigma_w$ leads to an almost constant value of $b$. The value of $b$ is calculated based on concurrent REA and EC measurements of a so-called proxy scalar such as water vapour, CO$_2$, and air temperature (e.g. Pattey et al., 1993; Pattey and Desjardins, 1999). Assuming similarity for the proxy scalar’s transport and the turbulent flux of trace gases, the value of $b$ calculated from the proxy scalar is used to determine the trace gas flux.
REA applications for isoprene using Teflon® bags as sampling reservoirs have been reported (Guenther et al., 1996; Pattey and Desjardins, 1999) though it is more common to sample BVOCs on adsorption tubes (Beverland et al., 1996a, b; Velentini et al., 1997; Christensen et al., 2000; Gallagher et al., 2000). Both experimental methodologies hold disadvantages, e.g. (1) necessity for a large number of adsorption tubes or bags in order to cover measurement campaigns of several weeks— in addition, this procedure requires careful handling of possible different properties of each tube or bag; (2) storage problems might mask the BVOC results and represent another possible technical flaw. The coupling of a REA sampler to in situ analyser for VOCs, including oxygenated VOCs (OVOCs) as described by Schade and Goldstein (2001) overcomes these two problems.

In this paper a REA technique for the determination of BVOC fluxes using an online gas-chromatographic (GC) technique and PTR–MS in parallel will be described and results from the BEWA2000 (Biogenic Emissions of Reactive VOC over Forests: Process, Modelling, and Validation Studies) field campaigns in July 2001 and 2002 will be discussed.

2. Experimental set-up

2.1. Site description

During the intensive field campaigns of BEWA2000 in the summers of 2001 and 2002, VOC measurements were conducted above a Norway spruce forest in a remote area of the German Fichtelgebirge (50°08′32″N, 11°52′04″O, 775 m a.s.l.), an area characterised by an alpine-like climate (Klemm and Mangold, 2001). A REA system was set up on a scaffolding tower with a sonic anemometer and with the inlet lines mounted 31 m a.g.l. on the uppermost platform of the tower. The forest around the tower consisted of approximately 19 m tall, 57-year-old Norway spruce trees (Picea abies L. [Karst.]). The greater fetch area was densely covered by older trees of the same species. The site and the instrumentation of the tower are described in detail by Klemm et al. (this issue).

Fig. 1 shows the experimental setup of the VOC–REA system. Basically, it consisted of three parts: (1) a commercial sonic anemometer; (2) a fast operating valve system including a real-time control system; and (3) an online GC device capable of sampling BVOC on adsorption tubes, with subsequent onsite sample analysis. In parallel to the GC instrument, a PTR–MS system for fast online VOC analysis (Hansel et al., 1995; Lindinger et al., 1998) was connected to the REA sampling system.

2.2. REA sampling system

The conditional sampling of our REA system was realised with two separate channels (up- and down-drought line) each consisting of a circa 30 m long Teflon® (PTFE) tube, a Furon® valve (PTFE, type DVX2-144-NC-D2, response time < 30 ms) close to the inlet (30 m platform), a 500 ml glass reservoir and a high grade steel valve (Bürkert—Germany, type 301, response time < 12 ms) at the bottom end of the REA system (4 m platform). Air samples were drawn by a pump at a rate of 101 min⁻¹. In previous studies (Steinbrecher et al., 2000) no tubing effects on VOC mixing ratios, even in case of 60 m long PTFE tubings, were observed. When the valves of the sampling line were opened a pressure drop of −350 hPa existed between the inlet and the high-grade steel valves.

If the line was closed, the pressure difference between the inside of the line and the ambient pressure was about −170 hPa. After opening the valves, fresh ambient air entered the line within only a few milliseconds. Thus, time delays were negligible. The valves at the inlet prevented air from entering the respective inactive line (up-line in case of down-draught and vice versa, both lines in the case dead-band) which otherwise would lead to an underestimation of the concentration differences and therewith the flux.

The sampling was determined at 10 Hz by a Gill sonic anemometer (Gill R350, UK) with an incorporated inclinometer. The anemometer data were recorded by a PC that accomplished the data acquisition and the valve triggering via a real-time Linux program. The criterion of valve switching was based on 5 min running mean values of σw updated on a 10 Hz basis. Valves were activated according to the current threshold condition |w| > 0.6σw. In the case of −w0 ≤ w ≤ w0, neither “up” nor “down” samples are taken, but a third high-grade steel valve (dead-band valve) was activated. The valve switching status (up-draught, down-draught or dead-band) was handed over from the PC parallel port to the valve switching system by a 5 V TTL signal. The valve switching system (24 V) controlled the Furon® valves as well as the high-grade steel valves. After 30 min data sampling, the program calculated...
Fig. 1. The set-up of the IMK-IFU GC–REA–system and the coupling with the Innsbruck PTR–MS. Main parts are the sonic anemometer for 10 Hz wind measurements, the REA valve system for sampling up and down draughts, and VOC analysis system (online GC and PTR–MS).
and saved data needed for REA calculations, i.e. the mean values of the wind vectors \( u, v, w \), and their corresponding standard deviations as well as mean values of the virtual temperature.

The calculation of the Businger–Oncley parameter, \( b \), was based on the vertical wind speed \( w \) and the virtual temperature \( T_v \). Both parameters were measured concurrently by the sonic anemometer. Based upon the chosen wind threshold of \( |w_0| = 0.6\sigma_w \), parameter \( b \) was determined for each accumulation period. In the BEWA field experiments average \( b \)-values were about 0.39.

The data acquisition program also allowed for calculating and saving mean values for an analogous output of an additional device, e.g. a hygrometer for the determination of fluxes of water vapour. The system was quality assured by concurrent flux determinations of water vapour using EC based on a KH20 Krypton Hygrometer (Campbell Scientific, UK) and this REA technique that had been adapted to the analytical requirements for water vapour sampling and measurement. Instead of adsorption tubes for VOC, 161 Tedlar bags were installed (sampling at a rate of 200 ml min\(^{-1}\) for 30 min). After sampling, the Tedlar bags were coupled to a differential infrared absorption device (BINOS, Rosemount, Germany) for subsequent analysis. Fig. 2 depicts results from this EC and REA comparison.

### 2.3. Online GC analysis

In this REA application an online GC system (HC1010, Airmotec, Germany) equipped with a flame ionisation detector (FID) was used for VOC analysis in up-draught and down-draught air samples. The HC1010 VOC analysis, including pre-concentration and cryo-focussing is detailed in Steinbrecher et al. (2000). For enhanced resolution a RTX 1701 capillary column (30 m \( \times \) 0.25 mm ID, 1.0 \( \mu \)m df; Restec, Germany) was used in this application. Extending the sampling time to 55 min yielded higher sample volumes of slightly more than 8 l, based on a sampling rate of

![Fig. 2. Comparison of water vapour fluxes determined by EC and REA methods.](image-url)
150 ml min\(^{-1}\), which improved the detection limit to 0.1 pptC.

2.4. Coupling of the REA sampling system and the online GC

As can be seen in Fig. 1, up- and down-draught lines had their own bypass system. Such a bypass system, as introduced by Christensen et al. (2000), enables a constant sampling rate for the sampling tubes, regardless of the valve switching frequency during the sampling period; Olofsson et al. (2005) recently presented a similar system. In both studies the sampling air was taken from reservoirs in the REA-lines, VOC were accumulated using adsorbent tubes and the gas stream was led back into the respective reservoir from the outlets of the mechanically adjusted sampling pumps. In our approach an online GC system was integrated into the bypass system with a flow rate kept at 150 ml min\(^{-1}\) by separate pumps and mass flow controllers. The sampling air was taken upstream of the glass reservoirs (500 ml) and re-introduced into the respective REA-line downstream of the reservoir (see Fig. 1). Long closure times of the sampling lines might lead to underestimations of the concentrations, since air samples that have already passed the GC analysis pathways would eventually re-enter this pathway. The maximal tolerable closure time was found to be 200 s. A series of tests feeding isoprene at constant volume mixing ratios (VMR) into both REA-lines—one continuously flushed (reference) and the other periodically activated (closure periods 90, 120, ... 480, and 1500 s)—substantiate this estimate. Fig. 3 shows that the isoprene values obtained for both lines overlap up to closure times of 210 s. For longer closure times the isoprene values obtained from the periodically closed sampling line significantly deviated from the reference values, indicating that air samples that had already been analysed re-enter the analytical pathway of the by-pass system. As a consequence, flux measurement data had to be screened for time periods with closure times of more than 200 s. These events were eliminated from the data set. Fortunately, in reality these events occur infrequently (typically in less than 1% of all cases). Christensen et al. (2000) and Olofsson et al. (2005) do not report on this potential error source. In the case of Olofsson et al. (2005) the maximal closure time

![Fig. 3. Dependence of the isoprene response factor on the closure time of the sampling line. The vertical line at 200 s denotes the maximum allowable closure time for this VOC–REA system.](image-url)
estimate is \( \sim 78 \) s; Christensen et al. (2000) do not specify their reservoir volume.

The uncertainty of the calculated isoprenoid fluxes were found to be \( \pm 0.3 \text{ nmol m}^{-2} \text{ ground surface s}^{-1} \) or \( \pm 10\% \), whatever is greater, assuming that the uncertainty of the GC VOC concentration analysis (\( \pm 10\% \)) primarily determines the overall VOC flux uncertainty.

2.5. PTR-MS system

PTR-MS is a fast detector for a broad range of VOC and allows the online monitoring of atmospheric trace gases like isoprenoids and oxygenated species. The principle of PTR-MS is described in detail by Hansel et al. (1995) and Lindinger et al. (1998).

A commercial PTR-MS instrument (PTRMS-FDT-s, Ionicon Analytik GmbH, Innsbruck, Austria) was used for the measurements. During the 2001 campaign the instrument was operated at standard operation conditions (\( E/N = 135 \text{ Td} \); \( E \) electric field strength, \( N \) buffer gas number density, \( 1 \text{ Td} = 10^{-17} \text{ cm}^2 \text{ V molecule}^{-1} \)). Operation at reduced \( E/N \) increases instrument sensitivity and reduces fragmentation of some of the anticipated target molecules (e.g. ethanol). In 2002 the PTR-MS instrument was thus operated at reduced \( E/N \) of \( \sim 100 \text{Td} \). The implications of nonstandard PTR-MS operation are described in detail by de Gouw et al. (2003) and Hewitt et al. (2003); sensitivity changes were studied in detailed calibration procedures (see below). The ion signal at \( m/e = 69 \) was exclusively attributed to isoprene, the ion signals at \( m/e = 81 \) and 137 were assigned to the sum of all monoterpene isomers (Tani et al., 2004). Methanol, acetaldehyde, acetone and the sum of the isomers methyl vinyl ketone and methacrolein were detected at \( m/e = 33, 45, 59 \) and 71, respectively.

On-site calibration of the PTR-MS systems was carried out for isoprene (10 ppbv isoprene in \( N_2 \) by SIAD, Bergamo, Italy), as well as for monoterpenes (10 ppbv \( \beta \)-pinene in \( N_2 \) and 10 ppbv limonene in \( N_2 \), both by SIAD VTG, Bergamo, Italy). In addition, an extensive laboratory intercomparison for hydrocarbons and carbonyls (VOC-mix in ppmv range in \( N_2 \), manufactured by E. Apel, NCAR, Boulder (CO), USA; ppbv ranges were obtained by subsequent dynamical dilution in humidified zero-air) was conducted in 2002 (Müller et al., this issue).

2.6. REA PTR–MS coupling

The determination of the average VMR in the REA-lines was done by successive measurements of the up-drought and down-drought line as suggested by Beverland et al. (1996b). The PTR–MS system was connected to the REA system via two Teflon® valves and short 1/8 in PFA lines (volume \( < 8 \text{ ml} \)), as shown in Fig. 1. This sampling unit drew samples from the up-draught line and down-draught line, respectively, and these air samples were alternately analysed by PTR–MS. Gas samples were drawn at a flow rate of less than 160 ml min\(^{-1}\). Measurement cycle time varied between 72 and 100 s. With this procedure 9–14 sample values per line were acquired within 30 min. All measured values of each half hourly period contributed to the half hourly mean value, \( \bar{x} \), of the VMR in the up-draught and down-draught lines, respectively. For each half hour mean value of each measured compound the 95% confidence intervals were calculated using the Student’s \( t \)-distribution, \( t_{n-1} \), and the experimental standard deviation, \( s_{n-1} \), of each dataset.

\[
\bar{x} \pm t_{n-1} \frac{s_{n-1}}{\sqrt{n}}.
\]  

The VMR mean values showed medial error margins ranging from 3.7% to 9.0%. The range of the error margin depended on the respective species and the variability of its VMR in the REA sampling lines. It is important to note that these margins of error are not a measure for the accuracy of the chemical analysis, but rather for the method of probing the REA lines alternately instead of accumulating continuously.

In 2001, the PTR–MS was connected to the REA-system at the lower end of the REA lines. In 2002, however, the PTR–MS system was set up on the 28 m platform of the scaffolding tower, drawing gas samples about 3 m downstream of the REA inlet valves and about 30 cm upstream of the ozone scrubbers.

3. Results

3.1. Turbulent fluxes of isoprenoids

Fig. 4c shows a diurnal pattern of the sum of the monoterpenes turbulent fluxes as measured by REA–PTR–MS during the 2001 campaign. As GC–FID data are not available for the given period, only PTR–MS data are reported. Data have been averaged over the period from 12:30 on 26 July to 03:30 on 3 August 2001. The dataset of the measured flux values is not complete over this period. Therefore, a varying number (2–6) of
individual half hourly values ($N = 2$ or $3$ only in the time segments $09:00$ to $10:30$, due to unfavourable conditions for REA-sampling or, in the case of August 2, due to malfunction of the PTR–MS system) contributed to the mean flux values of the respective half hourly period. The monoterpene fluxes showed a pronounced diurnal course with weak turbulent vertical transport—in most cases upward—in the night. During daytime, fluxes increased from the morning until mid-afternoon, when average flux rates reached their maximum of slightly more than $2\, \text{nmol m}^{-2}\text{s}^{-1}$. This coincided with the daytime maximum of photosynthetic active radiation (PAR; Fig. 4a), but occurred shortly before the daytime peak values for ambient temperature (Fig. 4b). Similar diurnal variations and monoterpene flux maxima were observed in 2002. Fig. 5c shows a time series of monoterpene flux rates as obtained by REA PTR–MS (solid circles) and REA GC–FID (open circles). PTR–MS cannot distinguish between C$_{10}$H$_{16}$ isomers. Therefore, fluxes of $\alpha$-pinene, camphene, $\beta$-pinene, and sabinene measured by REA GC–FID were summed up, enabling comparison of the results from both techniques. Good agreement was achieved for daytime measurements apart from a few outliers in the late afternoon on July 31. In a few cases during night-time, however, the GC technique determined negative flux rates up to a value of $1.5\, \text{nmol m}^{-2}\text{s}^{-1}$.

The reasons for these deviations are currently not understood and require further investigation. Daytime monoterpene flux rate maxima were found to be consistent with primary flux data derived from enclosure measurements ($0.50\, \text{m}^{-2}\text{h}^{-1}\text{g}^{-1}\text{d.wt.}$; (Grabmer et al., this issue)). The emission of monoterpene from trees in the fetch area around the tower was calculated using the common exponential algorithm (Guenther et al., 1993) and air temperature data which were found to be a good approximation of leaf temperature. At the tower site the leaf area index was $5.3$ (Klemm and Mangold, 2001) and the stand specific leaf weight was $175\, \text{g d.wt. m}^{-2}$ (Cojocariu et al., 2004). The conversion factor between total and projected leaf area was taken as $2.74\, \text{m}^{2}_{\text{tot.LA}}\text{m}^{2}_{\text{proj.LA}}$ according to Riederer et al. (1988) resulting in daytime monoterpene primary flux maxima of $2.3\, \text{nmol m}^{-2}\text{s}^{-1}$ based on an afternoon temperature of $\sim 27^\circ\text{C}$ as observed. Additionally, the experimental data could be reasonably well modelled using the coupled one-dimensional Canopy Atmospheric Chemistry Emission (CACHE) model (Forkel et al., this issue). Model data are represented in Fig. 5c as solid line.
Fig. 5d displays turbulent isoprene fluxes as measured by REA PTR–MS during the 2002 summer intensive field campaign. Due to some unknown coelutions which occurred at this site GC isoprene data could not be retrieved baseline resolved and is therefore not reported. Isoprene fluxes reached daytime maxima in the range of 1–1.5 nmol m$^{-2}$ s$^{-1}$. Again, experimental data are in good agreement with the CACHE model data shown as a solid line in Fig. 5d. Canopy fluxes were smaller than the primary fluxes calculated on the basis of enclosure measurements performed on Norway spruce twigs in the frame of BEWA2000 experiments which reached a maximum of 2.1 nmol m$^{-2}$ s$^{-1}$. The primary isoprene canopy flux was modelled using the emission algorithm by Guenther et al. (1995) implying a standard emission factor of 0.32 µg h$^{-1}$ g$^{-1}$ d.wt. (Grabmer et al., this issue), recorded air temperatures and PAR values, the latter one being corrected for canopy effects according to Norman (1979) as carried out by Forkel et al., this issue. This result supports the fact that some VOCs emitted from leaves are removed from the atmosphere inside the canopy and that only a fraction of primarily emitted VOC is transported through the canopy and released into the troposphere.

However, the difference between the primary fluxes and the fluxes measured above the canopy can only partly be explained by in-canopy chemical reactions. The simulations with CACHE permit to quantify the difference between primary fluxes and fluxes above the canopy due to in-canopy effects. Around noon of July 31 the potential flux simulated by CACHE was about 1.5 nmol m$^{-2}$ s$^{-1}$, i.e. 20% higher than the flux that was simulated and measured above the canopy.

### 3.2. Sampling artefacts for oxygenated VOC

The REA PTR–MS approach was tentatively applied for measuring also fluxes of OVOCs such as methanol ($m/z = 33$), acetaldehyde ($m/z = 45$), the sum of acetone and propanal ($m/z = 59$) and the sum of the isoprene oxidation products methyl vinyl ketone and methacrolein ($m/z = 71$). The REA sampling method used in our experiment, however, produced significant sampling artefacts for the given species. As an example, data resulting from a system malfunction in 2002 are shown in Fig. 6. The inlet valve of the down-draught line was blocked from about 09:00 CET onward and soon thereafter a significant increase of OVOCs in the line was observed. Especially, the first measurement cycle in every down-line sampling period showed very pronounced enhancements. This is, when air that had been residing in the MnO2 ozone scrubber and in the first few meters of the inlet line was sampled. In this study an experiment was performed to investigate artefact generation on the MnO2 ozone scrubber. The REA lines were kept open while air was sampled up- and down-stream the ozone scrubber for PTR–MS analysis. Measurements were carried out in the mid-afternoon with ambient ozone mixing ratios of ~58 ppbv. Ion signals at $m/z = 33$ (methanol), $m/z = 45$ (acetaldehyde), $m/z = 59$ (acetone and propanal) and $m/z = 71$ (here tentatively assigned to methyl vinyl ketone and methacrolein) showed relative enhancements in the range of 9–75 % downstream the ozone scrubber (Table 1). The unidentified ion signals at $m/z = 61, 101$ and 107 were also found to be significantly enhanced whereas ion signals at $m/z = 69$ (isoprene) and $m/z = 137$ (monoterpens) showed no significant change at all, downstream the scrubber. These findings indicate that the quality of isoprenoid measurements is not affected by reactions in the scrubber. Oxygenated compounds, however, are apparently strongly biased by scrubber interferences. Northway et al. (2004) recently pointed out a number of potential sources for OVOC artefacts, such as heterogeneous reactions of ozone with reactive organic compounds deposited onto inner surfaces of sampling systems and/or inlet lines, or heterogeneous reactions of ozone with the organic fraction of aerosols in the inlet system. Due to the sampling history of the REA lines, a varying contamination of inner surfaces cannot be excluded. This exhibits potential source for OVOC artefacts in addition to the scrubber interferences. These results clearly show that the REA PTR–MS approach used in this work is not suitable for artefact-free measurements of OVOCs. Also, they put further weight to the demand for a critical evaluation of OVOCs measurement in ambient air.

### 4. Conclusion

A REA device coupled to an online GC and a PTR–MS was used to determine isoprenoid fluxes above a Norway spruce forest in a remote area of the German Fichtelgebirge during the field campaigns of BEWA2000 in the summers of 2001 and 2002. The system was quality assured by concurrent
flux determinations of water vapour using EC and REA technique demonstrating good agreement between both methods. The maximum allowable closure time for the REA sampling lines was about 200 s and was exceeded infrequently during the field measurements. Test series showed that MnO2 ozone scrubbers do not bias the quality of isoprene and monoterpenes measurements. Significant artefacts were observed, however, for oxygenated species.

Measurements of turbulent fluxes of isoprenoids on selected days during the BEWA2000 field campaigns showed moderate diurnal variations. For monoterpenes maximum daytime fluxes were about 2 nmol m$^{-2}$ s$^{-1}$, isoprene fluxes reached 1–1.5 nmol m$^{-2}$ s$^{-1}$. The observed data agree reasonably well with primary flux data derived from enclosure measurements and results using the CACHE model. REA-systems coupled to online BVOC measurement devices that avoid sample storage in individual reservoirs are prospective tools for the assessment of net isoprenoid emissions.

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