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Quantification of interferences in PTR-MS measurements of monoterpene emissions from *Fagus sylvatica* L. using simultaneous TD-GC-MS measurements

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ABSTRACT

The interest in quantitative analysis of biogenic volatile organic compounds (BVOCs) emissions stems from their importance in atmospheric chemistry. In order to compare the most frequently used BVOC measurement techniques, simultaneous on-line PTR-MS and off-line GC-MS data collection was performed on a 3 years old *Fagus sylvatica* L. tree placed in a growth chamber. Using an internal standard (deuterated toluene) and applying the selective ion mode (SIM) resulted in significant improvements of monoterpene (MT) quantification by TD-GC-MS. PTR-MS quantification of MTs was based on the ion signal at *m/z* 137. In the course of the experiments the relative contribution of linalool compared to that of MTs was found to be up to 84%. Since this compound has also a PTR-MS signature at *m/z* 137, quantification of MT emission rates by PTR-MS was disturbed. Comparison of GC-MS and PTR-MS data allowed an estimation of the ratio of the PTR-MS sensitivity for linalool to the one for MTs at *m/z* 137. This ratio of sensitivities, combined with the information of the relative contribution of linalool to the sum of linalool and MTs obtained by GC-MS, resulted in accurate derivation of the sum of emission rates of linalool and MTs by PTR-MS. The results indicate that fast and on-line PTR-MS measurements of BVOCs are best accompanied by off-line GC measurements to detect possible interferences or to use the additional information for properly quantifying the sum of emission rates of several compounds.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are known to play an important role in tropospheric chemistry because of their high reactivity with the main atmospheric oxidants (OH, O_3, NO_3) [1]. BVOC oxidation can result in net oxidant formation and may lead to secondary organic aerosol (SOA) formation and/or growth [2,3], and as such affect regional air quality and global climate [4]. Although BVOC emission measurements already started a few decades ago, BVOC research continues to be an important topic in atmospheric and environmental sciences [5–11]. This continuing interest is being fed by new developments in analytical instrumentation, the need for long-term measurements and more data on the impact of environmental conditions and tree ecophysiology on BVOC emissions.

Gas Chromatography with Mass Spectrometry or Flame Ionization Detection (GC-MS, GC-FID) is one of the most popular techniques to monitor emissions into the atmosphere [12] with the advantage of compound separation, allowing for proper identification of the released volatiles and for individual compound calibration. When MS detection is selected, using an internal standard is highly recommended to compensate for variations in the detector response [13,14]. However, pre-concentration and time-integrated sampling are necessary. To monitor fast varying BVOC emissions, on-line Proton-Transfer Reaction-Mass Spectrometry (PTR-MS) is commonly used and has the advantages of high-sensitivity (no need for sample pre-concentration) and high temporal resolution [15–17]. In this case, the analysis and calibration of VOCs are based on a few selected ion signals, e.g. at *m/z* 137 for monoterpenes (MT). A few studies have been carried out on coupled GC-PTR-MS to investigate which compounds contribute to certain *m/z* ratios in PTR-MS [18]. A disadvantage of this method is that the ability of performing fast on-line measurements is lost. A few years ago Proton-Transfer Ion Trap-Mass Spectrometry (PIT-MS) was introduced by Prazeller et al. [19] (PTR-ITMS) and Warneke et al. [20] (PIT-MS). Although being less sensitive than PTR-MS, PIT-MS allows the differentiation of some isobaric compounds that cannot be distinguished by PTR-MS (e.g. methyl vinyl

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ketone and methacrolein, acetone and propanal). Recent laboratory PIT-MS measurements have shown that it is possible to distinguish between monoterpenes from the differences in Collision-Induced-Dissociation (CID) patterns of the estimator ions [21].

To compare the two commonly used techniques, GC-FID and PTR-MS measurements were carried out by Kato et al. [22] on several groups of compounds. Good correlation was found for hydrocarbon concentrations. However, the authors noted that the calculated PTR-MS data should be corrected by standard gas measurements. Similarly, Lee et al. [23] compared simultaneous measurements on 8 MTs, and observed 30% higher mixing ratios by PTR-MS, which was reduced to 20% by including 2 unidentified peaks in the GC-FID calculations. This observation highlights the importance of the detailed analysis of emission patterns and a better understanding of the fragmentation of contributing molecules in the PTR-MS. A detailed study by Tani et al. [24] of the fragmentation of 5 MTs, camphor and toluene in PTR-MS demonstrated the possibility to gain additional information in compound identification by varying the kinetic energy of the reactant ions. However, the authors concluded that simultaneous analysis by GC-FID/MS remains essential. A recent study [25] on methyl salicylate emission showed good agreement between GC-MS (400 ± 60 pptv) and PTR-MS (350 ± 40 pptv) in a branch enclosure experiment as well as in a direct comparison of flux measurements (GC-MS: 19 ± 5 pptv; PTR-MS: 24 ± 7 pptv).

In this paper we focus on quantification of emissions of monoterpenoid compounds, more specifically monoterpenes and linalool, by simultaneously using GC-MS and PTR-MS techniques. We emphasize how a lack of knowledge about the composition of the released volatiles can result in erroneous quantification by PTR-MS. Three practical solutions are presented to improve the correlation between BVOC emission results obtained by GC-MS and PTR-MS for *Fagus sylvatica* L.

2. Materials and methods

2.1. Experimental set-up

BVOC experiments took place in the framework of the project IMPECVOC (Impact of Phenology and Environmental Conditions on BVOC Emissions from Forest Ecosystems—http://www.impecvoc.ugent.be).

Measurements on a 3-year-old European Beech (*F. sylvatica* L.) were performed in a growth chamber between 27 August and 12 September in 2007. Temperature was varied between 17 and 27 °C and photosynthetic photon flux density (PPFD) was set stepwise to reach a maximum of 150 $\mu mol\ m^{-2}\ s^{-1}$ by using 40 fluorescent lamps (Master TL-D, Philips, 36 W/830 warm white, super 80).

To measure BVOC emissions, a dynamic branch enclosure system was used. A branch was selected from the middle of the tree and enclosed in a cuvette. The continuous air flow which was pumped into the cuvettes was scrubbed with a manganese dioxide (MnO_2) filter (ETO341FC003, Ansyco, and Karlsruhe, Germany) to remove ozone and with two activated charcoal filters (Airpel 10, Organosorb 10-CO, Desotec, Belgium) to remove VOCs. Ozone levels in the inlet air directly before the cuvettes were checked regularly by an ECC Ozonesonde (EN-SCI, Inc., Boulder, USA). Ozone concentrations were below 2 ppbv at all times. To minimize sorption of BVOC on the set-up materials, PFA foil and components in PFA or Teflon were used in the construction. The outlet of the cuvette was connected to the PTR-MS by 5 m long Teflon tube. Immediately after the outlet of the cuvette the line was split for a sampling point for the adsorbent tubes. This line was sealed by a PFA plug valve when no samples were taken.

2.2. GC-MS measurements

BVOCs were collected on multi-adsorbent tubes containing 210 mg Tenax TA ($35\ m^2\ g^{-1}$), Markes International, Llantrisant, UK) and Carbotrap ($100\ m^2\ g^{-1}$, 20–40 mesh, Markes International, Llantrisant, UK) with a volumetric ratio of 50:50. Before samples were collected, adsorbent tubes were conditioned at 300 °C under a He flow ($\sim 40\ mL\ min^{-1}$) for 1 h, then covered with aluminum foil and stored in a drier for a maximum of 7 days. Prior to sampling deuterated toluene (toluene-D8) was loaded on the tubes as an internal standard (ISTD) by a modified injection system to compensate fluctuations in the detector sensitivity [14]. Sampling was carried out at least 24 h after enclosure of the branches to minimize disturbance induced emissions [12]. Using a FLEC air sampling pump (FL-1001, Markes International, Llantrisant, UK) the flow was kept at $100\ mL\ min^{-1}$ for 5 min. Adsorbent tubes were analyzed within 24 h of sampling.

Desorption of the tubes was performed with an Ultra 50-50-UNITY thermal desorber (TD) and autosampler (Markes International, Llantrisant, UK). Separation was done by a GC Trace 2000 gas chromatograph (ThermoFinnigan, Milan, Italy) on a VF-1ms column (Varian, Sint-Katelijne-Waver, Belgium; 100% dimethylpolysiloxane; $30\ m \times 0.25\ mm \times 1\ \mu m$). A MS Trace DSQ WE-250 mass spectrometer (ThermoFinnigan, Austin, TX, USA) equipped with electron impact (EI) ionization was used for detection. The MS detector was operating in an alternating TIC-SIM mode, with a scan range of *m/z* 45–222 in the total ion current (TIC) mode. Quantification was based on the SIM mode, where *m/z* 91, 93, 121 ions were selected for MTs, *m/z* 53, 67, 68 for isoprenoids, *m/z* 98, 100 for toluene-D8 and *m/z* 69, 93, 204 for sesquiterpenes (SQTs). Peaks were only quantified if they were above the limit of detection (LOD) in TIC mode, which was based on the 3:1 signal to noise ratio.

Calibration of the GC-MS was performed monthly using 2 gas standard mixtures. The first mixture (Apel-Riemer Environmental in Denver, CO), hereafter referred to as calibration mixture A, contained methanol (1.01 ppmv), ethanol (1.01 ppmv), acetone (1.01 ppmv), isoprene (0.52 ppmv), sabinene (0.41 ppmv) and α-pinene (0.47 ppmv) with an uncertainty of <5% in nitrogen gas (mixture *A*). A second mixture (Apel-Riemer Environmental in Denver, CO), referred to as calibration mixture B and including isoprene (0.515 ppmv), α-pinene (0.496 ppmv), β-pinene (0.501 ppmv), sabinene (0.492 ppmv), limonene (0.486 ppmv), linalool (0.473 ppmv) and (Z)-3-hexenyl-acetate (0.499 ppmv) was prepared later and used for the calibration of linalool afterwards. Flows with different concentrations were realized by diluting the calibration mixtures with zero-air (IEC 1001 Zero Air Generator, Parker Balston, and Haverhill, MA, USA). For the quantification of those terpenes that were not available in the gas standard, response factors of sabinene were used.

2.3. PTR-MS measurements

On-line BVOC measurements were performed with a commercially available high-sensitivity PTR-MS instrument (Ionicon Analytik GmbH, Austria). The technique is based on fast chemical ionization of VOCs by the proton-transfer reaction with hydronium (H_3O^+) ions in a medium pressure flow/drift tube reactor. The principle of operation of the technique and instrumental details have been described in detail in the literature [26–28] and therefore only the features of interest to the present study will be discussed.

The PTR-MS was operated at a reactor pressure of 2.34 hPa and a drift voltage of 600 V, resulting in an *E/N* value of 128 Td ($1\ Td = 10^{-17}\ V\ cm^2$), with *E* the electric field and *N* the ambient air number density in the flow/drift tube reactor. When ambient air is pumped through the reactor, the hydronium ions exiting

the ion source compartment undergo clustering reactions with water vapor molecules. This results in a proton hydrate distribution ($H_3O^+ \cdot (H_2O)_n$, $n = 0, 1, 2, \ldots$) in the flow/drift tube that depends on the E/N value, as well as on the relative humidity of the air to be analyzed. At the E/N value used in the present experiments, however, the contribution of H_3O^+ ions to this proton hydrate distribution is higher than 90% for water vapor pressures up to 22.1 hPa. Moreover, high E/N values inhibit the formation of water clusters of protonated VOCs. Suppression of the formation of both reactant ion and product ion water clusters facilitates mass spectral interpretation.

In PTR-MS analysis the mixing ratio X_{VOC} of the reactant VOC in ambient air is given by Eq. (1), with P_m^n the normalized fingerprint product ion signal of the VOC, expressed in normalized counts per second, and $S_{VOC,m}$ the sensitivity of the instrument for detection of the VOC based on the H_3O^+/VOC reaction product at mass m and expressed in normalized counts per second per ppbv (parts per billion by volume). Normalization refers to the product ion count rate that would be obtained at a reactant H_3O^+ count rate of 10^6 counts per second.

$$X_{VOC} = \frac{P_m^n}{S_{VOC,m}} \quad (1)$$

The normalized product ion signal P_m^n in Eq. (1) is given by Eq. (2), in which P_m and R_{21} are the count rates of the VOC product ion at mass m and of the isotope of the reactant H_3O^+ ion at m/z 21, respectively.

$$P_m^n = \frac{P_m \times 10^6}{R_{21} \times 500} \quad (2)$$

The sensitivity factor $S_{VOC,m}$ in Eq. (1) can be obtained from first principles, taking into account the rate constant k and the product ion distribution (PID) of the H_3O^+/VOC reaction. Both the lack of kinetic and mechanistic information on ion/VOC chemistry at different environmental (e.g. relative humidity) and instrumental (e.g. E/N) conditions and uncertainties on experimentally determined rate constants (mainly obtained in thermal conditions) result in an error on $S_{VOC,m}$ which can be as high as 30%. As a result it has become common practice in the PTR-MS community to determine the sensitivity factors by calibrating the instrument against dilute mixtures of the VOCs in an inert gas, with mixing ratios which can be as accurate as 5%. For the present experiments calibration mixture A (see Section 2.2, paragraph 3) was used to calibrate the PTR-MS for the sum of two monoterpenes (α-pinene and sabinene), based on the ion signal of m/z at 137. Monoterpene mixing ratios between 0 and 12 ppbv were obtained by dynamic dilution of the calibration gas in a VOC-free air flow. This calibration assumes equal PTR-MS sensitivity for α-pinene and sabinene, i.e. equal rate constants and PIDs for the reactions with H_3O^+. Calibrations of the PTR-MS were performed weekly in order to account for deterioration of detector performance.

3. Results and discussion

3.1. Quality control of the GC-MS measurements

3.1.1. Quantification from SIM mode

Due to the low concentrations of BVOC and with the aim of eliminating background peaks from the chromatograms, the SIM mode was employed for quantitative information of the emitted volatiles. The signal to noise ratio (S/N) determined for sabinene (9.837 ng/tube) in the SIM mode was 64 times higher than the one measured in the TIC mode. Limit of detection (LOD) and limit of quantification (LOQ) were defined as 3 and 10 times of the noise respectively, and were calculated both in TIC and SIM mode. Results for sabinene showed that the LOQ in SIM (0.047 ng) was approximately 20 times better than LOD in TIC (0.887 ng). Therefore quantification based on the SIM mode was beneficial for the measurement of MT in low concentrations.

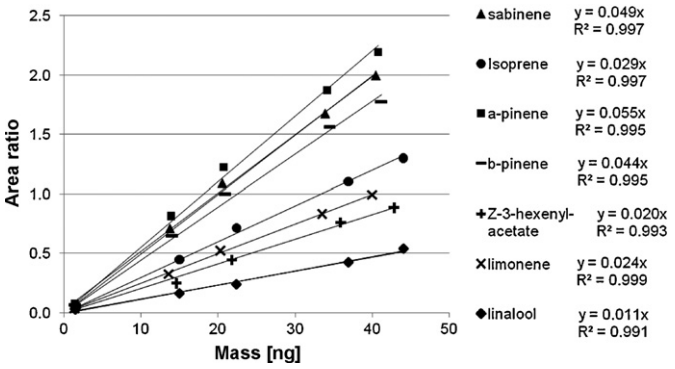

Fig. 1. Calibration curves and relative GC-MS response factors for the different compounds obtained by using the gas standard mixture B. Concentrations were varied by changing the dilution flow. Area ratios are defined as the integrated peak area divided by that of the internal standard (toluene-D8) based on SIM measurements (toluene-D8: m/z 98 and 100; isoprene: m/z 53, 67 and 68; remaining compounds: m/z 91, 93 and 121).

3.1.2. Stability of the EI-MS

In order to compensate for the drift of the electron impact MS sensitivity in time, toluene-D8 was applied as an internal standard. The relative standard deviation (RSD) of toluene-D8 determined for the samples used for the comparison of PTR-MS and GC-MS measurements was 8.4% ($n = 23$). A decrease of the integrated areas was found over the 18 days measurement period.

To test the precision of the sampling procedure 3 repeated samples were taken in sequence at the same PPFD and temperature conditions in the growth chamber. RSDs of areas and area ratios were compared for all detected compounds in order to verify the usefulness of the ISTD. Improvement in RSDs was realized when using the internal standard, and resulted 4.4–18.8% RSDs in the BVOC emission samples. RSDs increased with decreasing compound concentrations.

3.1.3. Calibration of individual BVOC with GC-MS

In this study, the use of gas standard mixtures enabled proper calibration for isoprene, α-pinene, β-pinene, sabinene, limonene, linalool and (Z)-3-hexenyl-acetate. Linearity of the 5-point calibration curves was checked in the range of 0–45 ng. Statistics showed highly significant linear relationship ($P < 0.001$) and no significant difference of the intercept from zero (P between 0.105 and 0.595). The variation in relative response factors (RRF), which takes into account the normalization with the ISTD, is given in Fig. 1, where a factor of 4.5 difference was found between sabinene and linalool using the same SIM mode (m/z 91, 93, 121). To investigate if this factor of 4.5 difference mainly originates from the difference in EI ionization efficiencies or rather from the different fragmentations of the compounds, the contribution of the fragmentation effect was calculated in the following way. The 10 most abundant fragment ions and the ions used in the SIM mode were selected both for sabinene and linalool. After summing the relative abundance of these fragment ions (ΣI_x(TIC)), and comparing them with the sum of the selected ions used in the SIM mode (ΣI_x(SIM)), one could conclude that the selected ions at m/z 91, 93, 121 make up 43% of all the fragment ions for sabinene, which is 19% in the case of linalool. As a result, a factor of 2.2 out of the 4.5 difference in RRFs is explained by the different fragmentation of the molecules, using m/z at 91, 93 and 121 for quantification. The remaining difference is attributed to the different EI ionization efficiencies and instrumental parameters. Division of ΣI_x(SIM)/ΣI_x(TIC) by the RRF values

for each of the four commonly emitted monoterpenes resulted in the same value (with a RSD of only 4%). Therefore, one could conclude that the variation in the hereby obtained RRF values between these monoterpenes is mainly determined by the fragmentation of the individual compounds, and that the effect of EI ionization efficiency and other instrumental parameters is negligible. In conclusion, one should be cautious when summarizing emissions of several compounds using the same response factor for all individuals. When using for instance an averaged response factor of MTs or the one of sabinene for linalool quantification by lack of a proper calibration standard for this compound, linalool emissions quantified from the TIC mode would be underestimated by a factor of 2.

3.2. Growth chamber measurements on Fagus sylvatica L.

During the measurement period, 23 samples were analyzed by GC-MS, excluding repeated samples that were used for quality control. Temperature and PPFD were varied artificially and resulted in different concentrations of BVOC emission. Three monoterpenes (sabinene, (E)-β-ocimene and an unknown MT), linalool, a homoterpene identified as (E)-4,8-dimethyl-1,3,7-nonatriene (DMNT) and α-farnesene were identified from the emission of *F. sylvatica* L.

3.2.1. Contribution of linalool

Unexpectedly high emission, up to 1.86 $\mu g\, g_{dw}^{-1}\, h^{-1}$ of linalool was observed by GC-MS in the course of the measurement campaign (Fig. 2). This observation was found to be critically important when monitoring MT emissions by PTR-MS based on the ion signal at *m/z* 137 (see Section 3.2.2). Therefore, the sum of MT emission rates was compared with that of linalool. An average relative contribution of linalool to the sum of linalool and MTs of 29% increased up to 84% by the end of the measurement period. Looking at the sum of emission rates of linalool and MTs, one can conclude that the high contribution of linalool is not directly related to higher overall BVOC emissions. Linalool emission was found to result from infection of the trees with the aphid *Phyllaphis fagi* L. [29].

Previously, linalool emissions have been mentioned a few times in connection to *F. sylvatica* L. [30], *Abies religiosa* and *Pinus patula* [7] in amounts up to 0.2%, 3% and 18% of total measured BVOC respectively. In a seasonal study Hakola et al. [8] found linalool emissions from Scots Pine, with peak values in July, up to 64 $ng\, g^{-1}_{(needledryweight)}\, h^{-1}$ expressed in standard conditions of 1000 $\mu mol\, m^{-2}\, s^{-1}$ and 30 °C. However, it still remains a minor part of the total BVOC emissions (1%).

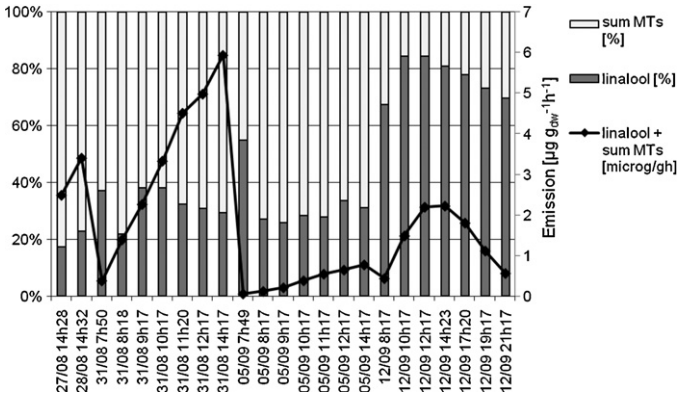

Fig. 2. Relative contribution of linalool to the sum of linalool and monoterpenes for all enclosure air samples taken from *Fagus sylvatica* L. during the experimental period. Results are based on GC-MS measurements. Also shown are absolute linalool + monoterpene emission rates in $\mu g\, g_{dw}^{-1}\, h^{-1}$.

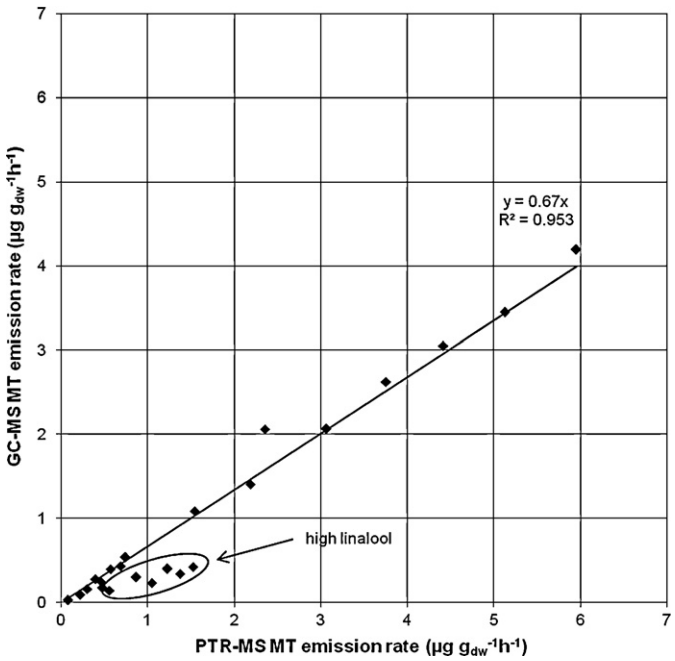

Fig. 3. Measured GC-MS monoterpene emission rates versus those obtained by PTR-MS when assuming that no other compounds than monoterpenes contribute to the PTR-MS ion signal at *m/z* 137 (see text for more explanations). The largest deviations from the linear relationship (encircled data points) correspond to the highest contributions of linalool.

3.2.2. Correlation between PTR-MS and GC-MS measurements

Continuous quantitative measurements of MT with PTR-MS are generally obtained by monitoring the ion signal at *m/z* 137, corresponding to protonated MT ($C_{10}H_{17}^+$). Accurate quantification, however, assumes the absence of other compounds which give rise to a protonated molecular ion or to a fragment ion at the same *m/z*. It also depends on how similar the MT compositions in the sample and in the calibration mixtures are, since different MTs can have different response factors. The aim of the GC-MS/PTR-MS intercomparison exercise was to find out whether the PTR-MS signal at *m/z* 137 is indeed a good estimator for quantification of monoterpene emissions by *F. sylvatica* L. trees.

In Fig. 3 the measured MT emission rates based on GC-MS are plotted against those obtained from the PTR-MS signal at *m/z* 137. For the PTR-MS MT emission rates, a sensitivity factor $S_{MT,137}$ as determined by means of calibration mixture *A* was taken into account. Linear regression resulted in a slope of 0.67 ($R^2 = 0.953$) and the PTR-MS MT emission rates were roughly twice as high as the GC-MS ones when the highest linalool contributions were observed.

As mentioned in Section 3.2, however, several terpenoid species were identified in the course of the measurement campaign with the GC-MS technique. The major contributors were found to be monoterpenes (mainly sabinene) and linalool. Since the product ion distribution of the H_3O^+/linalool reaction [17,31] is very similar to the one of the H_3O^+/monoterpene reactions [17,24,32,33], ions at *m/z* 137 cannot be considered as a specific estimator for MTs in the branch enclosure experiments. Consequently, the ion signal at *m/z* 137 should be considered as an indicator of monoterpenoid emission (mainly MTs and linalool) rather than of MT emissions solely. It should be noted that the introduction of linalool in the PTR-MS also results in the protonated product ion at *m/z* 155. At the operational conditions of the PTR-MS in the present study, however, the yield of this product ion is very small and quantification of linalool emissions from the *F. sylvatica* L. tree based on the ion signal at this

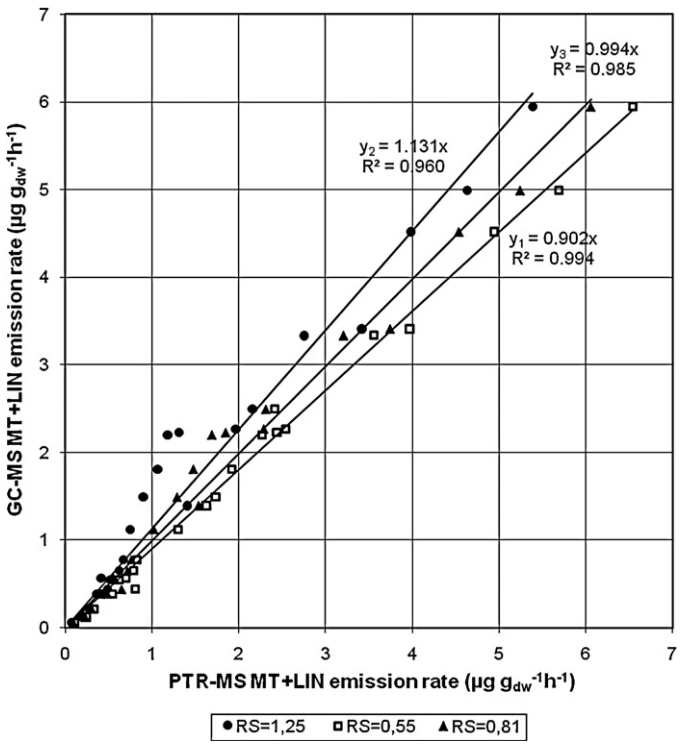

Fig. 4. Comparison of GC-MS and PTR-MS emission rates of the sum of monoterpenes (MT) and linalool when taking into account a weighted PTR-MS sensitivity factor. RS is the ratio of the PTR-MS sensitivities of linalool and MTs based on the ion signal at *m/z* 137 ($S_{LIN,137}/S_{MT,137}$).

m/z would be highly inaccurate. Therefore, in what follows, we will focus on the PTR-MS ion signal at *m/z* 137.

Since none of the calibration bottles (*A* and *B*) available during the growth room experiments contained linalool in the absence of MTs, the PTR-MS sensitivity factor for linalool based on ion signals at *m/z* 137, $S_{LIN,137}$, could not be obtained in a direct way. This factor was therefore inferred in an empirical way through comparison of the sum of emission rates of monoterpenes and linalool derived from GC-MS measurements, $Q_{MT+LIN,GC-MS}$ [$\mu g\, g_{dw}^{-1}\, h^{-1}$], and from PTR-MS measurements, $Q_{MT+LIN,PTR-MS}$ [$\mu g\, g_{dw}^{-1}\, h^{-1}$]. The latter is given by Eq. (3):

$$Q_{MT+LIN,PTR-MS} = \frac{C}{B} \times \frac{P_{137}^{n}}{S_{MT,137}} \times \frac{(F_{MT}M_{MT} + (1 - F_{MT})M_{LIN})}{F_{MT} + (1 - F_{MT}) \times (S_{LIN,137}/S_{MT,137})} \quad (3)$$

This equation takes into account a weighted sensitivity factor for monoterpenoid quantification by PTR-MS based on the ion signal at *m/z* 137 and a weighted monoterpenoid molar mass. F_{MT} is the relative contribution of monoterpenes to the sum of monoterpenes and linalool, as determined from the GC-MS measurements, *B* is the enclosed biomass dry weight (g), and *C*, given by Eq. (4), is the conversion factor from mixing ratios (measured by PTR-MS) to VOC molar flow rates from the enclosed branch.

$$C = \frac{3600}{10^6} \times \frac{Q_0}{RT_0} \quad (4)$$

In Eq. (4), Q_0 [$Pa\, m^3\, s^{-1}$] equals the flow rate of VOC- and O_3-free air through the cuvette at standard conditions of pressure (101.325 kPa) and temperature (273.15 K), *R* is the ideal gas constant (8.314 $J\, mol^{-1}\, K^{-1}$) and T_0 equals 273.15 K.

In the first approach linear regression was applied on the $Q_{MT+LIN,GC-MS}$ versus $Q_{MT+LIN,PTR-MS}$ data points. A maximal R^2 value (0.994) was obtained at a $S_{LIN,137}/S_{MT,137}$ ratio of 0.55. As shown in Fig. 4 (y_1), this reduces the deviation between PTR-MS and GC-MS from 33% to 10%.

In the second step the ratio $S_{LIN,137}/S_{MT,137}$ is expressed in terms of the characteristics of the involved ion/molecule reactions in Eq. (5) at the operating conditions of the PTR-MS instrument. $Y_{X,137}$ denotes the contribution of the $C_{10}H_{17}^+$ ion species in the PID of the H_3O^+/X reaction (branching ratio).

$$\frac{S_{LIN,137}}{S_{MT,137}} = \frac{k_{LIN} \times Y_{LIN,137}}{k_{MT} \times Y_{MT,137}} \quad (5)$$

By taking into account rate constant data from the literature [31,33], obtained in thermal conditions with a Selected Ion Flow Tube instrument, k_{LIN}/k_{MT} is found to be 1.25. When assuming that the difference in sensitivity for detection of MTs and linalool would be entirely due to the difference in rate constants for the reaction with H_3O^+ ions, i.e. when setting $S_{LIN,137}/S_{MT,137}$ equal to k_{LIN}/k_{MT}, data corresponding to high contributions of linalool show a strong deviation from the linear fit through all data points (Fig. 4; y_2). In this case a slope of 1.131 with the R^2 of 0.960 was obtained with higher values for the GC-MS.

As the GC-MS measurements indicated that sabinene was the most abundant monoterpene, a better estimation of $S_{LIN,137}/S_{MT,137}$ could be obtained by experimental derivation of $Y_{LIN,137}/Y_{SAB,137}$. Therefore, in the third approach, PTR-MS spectra at identical instrumental conditions were subsequently taken of pure linalool, pure α-pinene and of calibration mixture *A* (containing the MTs α-pinene and sabinene), all diluted in VOC-free air before introduction in the instrument. From these data, values of 0.41, 0.47 and 0.30 were obtained for $Y_{\alpha\text{-pinene},137}$, $Y_{SAB,137}$ and $Y_{LIN,137}$, respectively. These are somewhat smaller than the values of 0.47, 0.52 and 0.41 that were obtained by Tani et al. [34] for the respective branching ratios, which might be attributed to the uncertainty on the experimentally determined mass discrimination of the instruments. Our data result in a $Y_{LIN,137}/Y_{SAB,137}$ ratio of 0.65, and consequently in a $S_{LIN,137}/S_{MT,137}$ value of 0.81 (Fig. 4; y_3). This ratio is about 50% higher than the empirically determined value of 0.55. A possible explanation could be an overestimation of k_{LIN}/k_{MT}. Tani et al. [34] found k_{MT} in PTR-MS conditions to be identical to the values measured in thermal flow tube instruments. However, no data are available on the *E/N* dependence of k_{LIN}. On the other hand the best correlation was found for the two instruments in this case with a slope of 0.994 (R^2 = 0.985).

Although the PTR-MS ion signal at *m/z* 137 in the *F. sylvatica* L. branch enclosure experiments is expected to result mainly from emissions of monoterpenes and linalool, a small fraction of this ion signal may be due to the emission of α-farnesene, a sesquiterpene (SQT) which has also been observed by GC-MS. Limitations in the calibration of SQT in GC-MS, however, result in an inaccurate estimation of the contribution of α-farnesene to *m/z* 137. Recent studies of PTR-MS product ion distributions have shown indeed that SQTs can also result in a fragment ion at *m/z* 137 [35,36]. In a limited study on four SQTs [36], the highest product ion yield at *m/z* 137 was found for β-caryophyllene (6%). Taking into account this value, the abovementioned values for the product ion yields of the MTs and linalool, a calculated value for the rate constant of the H_3O^+/SQT reaction, and estimated sesquiterpene emission rates based on GC-MS quantification, the PTR-MS ion signal at *m/z* 137 due to SQTs is expected to account for only 3% of the total *m/z* 137 ion signal. Therefore, the emission of SQTs most probably affects PTR-MS based monoterpenoid emission rate measurements only to a small extent.

4. Conclusion

Biogenic volatile organic compound emissions were measured by GC-MS and PTR-MS from a 3-year-old potted *F. sylvatica* L. tree.

Six compounds were identified including 3 MTs (sabinene to be the most abundant), linalool, a homoterpene identified as (E)-4,8-dimethyl-1,3,7-nonatriene (DMNT) and α-farnesene.

Several aspects related to quality control of the GC-MS measurements were considered. The use of the internal standard toluene-D8 was found to improve the RSD of the samples. Furthermore, the application of the selective ion monitoring (SIM) mode improved the *S*/*N* ratio of sabinene by a factor of 64 compared to that of the total ion current (TIC) mode, and consequently resulted in a sensitive quantification of the MTs at low concentrations. The importance of having the individual compounds for calibration was emphasized. More specifically it was found that using an averaged response factor of monoterpenes for quantifying linalool emissions in the TIC mode could result in an underestimation by a factor of 2, mainly due to different EI ionization efficiencies.

By being a very fast and sensitive on-line analyzer, a PTR-MS occupies a unique position in VOC research. However, quantification of individual VOCs by PTR-MS can be hampered by the absence of a unique estimator ion for the compound of interest due to overlapping *m/z* ratios of ion signals originating from several VOCs that are present in the air sample.

Monoterpenes have been measured by PTR-MS on many occasions by several research groups and the PTR-MS ion signal at *m/z* 137 ($C_{10}H_{17}^+$) has always been considered as a good estimator ion for the sum of MTs, as was sometimes verified by complementary GC measurements.

The results that were obtained in the present work show that one should remain cautious when quantifying MT emissions from vegetation by PTR-MS based on the ion signal at *m/z* 137. Indeed, GC-MS measurements of BVOC emissions from the *F. sylvatica* L. tree revealed high emissions of the oxygenated MT, linalool. Since linalool also has a PTR-MS signature at *m/z* 137, its presence artificially increased PTR-MS emission rates of MTs (up to a factor of 2 in extreme conditions) that were obtained by taking into account the PTR-MS sensitivity factor for MTs at *m/z* 137 ($S_{MT,137}$). The latter was determined using a gravimetrically prepared gas mixture containing two MTs (α-pinene and sabinene).

By comparing GC-MS and PTR-MS data, the ratio of the PTR-MS sensitivity factor for linalool ($S_{LIN,137}$) to the one of MTs (mainly sabinene), i.e. $S_{LIN,137}/S_{MT,137}$, was obtained by using an empirical statistical approach and by an approach which took into account the characteristics of the individual ion/molecule reactions of these compounds with H_3O^+. When taking into account the ratio determined with the latter approach, as well as the information obtained with GC-MS on the relative contributions of linalool and MTs to the sum of monoterpenoids, a weighted PTR-MS sensitivity factor was obtained which could be applied for accurate quantification of the sum of emission rates of MTs and linalool by PTR-MS.

The final conclusion of this GC-MS/PTR-MS intercomparison exercise is that PTR-MS measurements should preferably be accompanied by regular GC-MS measurements. The information, obtained with GC-MS, on the relative contribution of the different compounds that have a signature at the same *m/z* value as the target compound, can be used to determine a weighted sensitivity factor for the sum of the target and interfering compounds. Depending on the research objectives fast on-line quantification of this sum of compounds by PTR-MS can still be very meaningful.

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