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Technical note: Interferences of volatile organic compounds (VOC) on methane concentration measurements

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Abstract. Studies that quantify plant methane (CH_4) emission rely on the accurate measurement of small changes CH_4 concentrations that coincide with much larger changes in the concentration of volatile organic compounds (VOCs). Here, we assessed if 11 commonly occurring VOCs (e.g., methanol, α- and β-pinene, Δ3-carene) interfered with CH_4 concentrations measurements by five laser absorption spectroscopy and Fourier-transformed infrared spectroscopy (FTIR) based CH_4 analysers, and quantified the interference of seven compounds on three instruments. Our results showed widespread interfere of VOCs with FTIR based CH_4 analysers, but only minimal interference with laser absorption spectroscopy based analysers. VOCs not included in the spectral library exerted a strong strong (64 - 1800 ppb apparent CH_4 / ppm VOC) bias on FTIR based measurements, which can lead to substantial over- and underestimations of CH_4 fluxes. Minor (0.7 - 126 ppb / ppm) interference with FTIR based measurements were also detected when the spectrum of the interfering VOC was included in the library. In contrast, we detected only minor (<20 ppb / ppm) and transient (<1 minute) VOC interferences on laser absorption spectroscopy based analysers. Our results thus suggest that FTIR based instruments are not well suited for quantifying plant CH_4 emissions. However, our results also suggest that FTIR can precisely quantify VOC concentrations, and could therefore provide a method complementary to proton-transfer-reaction mass spectrometry (PTR-MS).

1 Introduction

Gas analysers based on infrared spectroscopy are increasingly used to study fluxes of CH_4 and other trace gases in natural and anthropogenic ecosystems (e.g. Zellweger et al., 2016; Etiope, 2015; Rapson and Dacres, 2014). Laser absorption spectroscopy based on cavity ring-down spectroscopy (CRDS) or off-axis integrated cavity output spectroscopy (OA-ICOS) is currently considered state of the art by international flux stations networks (Franz et al., 2018). These analysers quantify trace gas concentrations through absorption at one specific wavelength. Fourier-transformed infrared spectroscopy (FTIR) is another approach to measure greenhouse gas fluxes that is gaining popularity because of lower costs, easier field portability, and great versatility with regards to target compounds analystes (Warlo et al., 2018; Teutscherova et al., 2019; Kandel et al., 2018). FTIR

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based analysers measure a complete infrared absorption spectrum, and then quantify the concentrations of trace gases through spectral deconvolution using reference spectra for a number of potentially present gases. The capabilities and limitations of both instrument types remain subject of ongoing research. In particular, the potential for biased measurements due to spectral interference with other gases still needs to be established for various environments and applications (e.g. Rella et al., 2015; Assan et al., 2017; Zhao et al., 2012; Zellweger et al., 2016).

Plants were recently identified as an important component of the natural cycles of CH_4 (Keppler et al., 2006; Nisbet et al., 2009; Carmichael et al., 2014). This has led to an increased interest in the role of trees in the CH4 exchange of forests (e.g. Pangala et al., 2017, 2015; Machacova et al., 2016; Pitz et al., 2018; Pitz and Megonigal, 2017). Such studies require precise measurements of CH_4 emissions from tree stems and shoots, which are typically conducted using the static chamber method where part of a plant (typically shoots or stem areas) places in an enclosure and changes in CH_4 concentrations over time are monitored (Covey and Megonigal, 2019). This monitoring of CH_4 concentrations was traditionally conducted by collecting chamber air samples at different time points, which were then analysed by gas chromatography (e.g. Machacova et al., 2016). More recently, portable analysers based on CRDS, OA-ICOS or FTIR are increasingly used to measure chamber air CH_4 concentrations directly in the field (Warner et al., 2017; Pitz and Megonigal, 2017; Pitz et al., 2018). These novel methods have facilitated easier, faster, and more precise measurements of CH_4 fluxes, but have also increased vulnerability towards mismeasurements due to spectral interferences. This is especially important in the study CH_4 emissions by plants as plants co-emit a variety of volatile organic compounds (VOC) along with CH_4 which have a high potential to interfere with CH_4 analysis given that these VOC can be emitted at rates 2 to 4 orders of magnitude higher than currently reported CH_4 (Rinne et al., 2002; Simpson et al., 1999; Tarvainen et al., 2005; Machacova et al., 2016; Pangala et al., 2017). The degree to which plant-emitted VOCs interfere with CH_4 concentration measurements, however, has so far not been evaluated.

In a recent field campaign, we conducted parallel measurements of tree stem CH_4 emissions with two distinct methane analysers (Los Gatos Research (LGR) UGGA and GASMET DX4040). The two analysers gave contradicting results, with apparent CH_4 fluxes differing both in direction and in magnitude (Fig 1). We hypothesized that these divergent measurements resulted from interferences of VOCs with CH_4 measurements. To test this hypothesis, we built a setup to quantify the effect of eleven different VOCs on five commonly used CH_4 analysers under controlled conditions.

2 Methods

2.1 Field measurements

Field measurements were conducted as part of a larger field campaign in the Skogaryd research forest in southern Sweden (58°23'N, 12°09'E) (Klemedtsson et al., 2010) in the Summer of 2018. We measured stem CH_4 emissions from 30 trees at different distances from the main ditch to achieve a gradient of water table levels. The trees were equipped with box chambers to measure stem gas exchange as described in Machacova et al. (2016). CH_4 emissions were measured by closing chambers for 20 minutes and recycling air through one of two portable CH_4 analysers, a Los Gatos Research (LGR) UGGA (OA-ICOS based) and a Gasmet DX4040 (FTIR based). CH_4 exchange rates were quantified as the increase in CH_4 concentration over time, divided by the chamber volume and the stem area. Negative fluxes indicate a net CH_4 uptake and positive fluxes a net CH_4 release to the atmosphere. Measurements were conducted daily from June 2^{nd} to 13^{th} and from July 25^{th} to August 5^{th} 2018, alternating between the two instruments.

2.2 Laboratory tests 1 – Qualitative screening for VOC interferences

In a first series of experiments, we qualitatively screened for VOCs that interfered with CH_4 analysers. We constructed an experimental system where VOCs can be added to a air stream with constant CH_4 concentrations (Fig. 3a). Air from the in-house pressured air supply was first passed through a membrane drier (SMC IDX-series) and a zero-air generator (HPZA 3500 220, Parker Balston) to remove any VOCs present in the background air. Due to a defect, the zero-air generator did not remove CH_4 from the air source, such that atmospheric CH_4 concentrations were present in the air used for our experiments. The flow air was then passed through a needle valve and a flow meter to set and monitor its flow rate. Next, we used two electronic three-way solenoid valves (SMC VX3-series) operated through a python script to guide the air flow either through a VOC source or a bypass line. The VOC source was an open or partly open vial of a pure VOC standard in a 500 mL glass bottle. The air flow was alternatingly set to the VOC source and bypass for 2.5 minutes. Finally, the air flow was passed to six instruments and an overflow outlet through T-connectors. All wetted parts of the air line after the zero-air generator were either stainless steel, PTFE or glass to prevent generation or removal of VOCs in the air flow path.

The flow rate of air entering the system was set slightly above the total air intake of all analysers (approximately 5 L min^{-1}). We tested four analysers based on laser spectroscopy (CRDS), including two stationary instruments (Picarro G2301 (CO_2, CH_4, H_2O); Picarro G2201i ($^{13}CO_2$, $^{13}CH_4$, H_2O) and two portable instruments (Picarro G4301; LGR UGGA (CO_2, CH_4, H_2O)), as well as one analyser based on Fourier-transformed infrared (FTIR) spectroscopy (GASMET DX4015). For control, we quantified VOC concentrations by proton transfer reaction quadrupole mass spectrometry (PTR-MS, Ionicon Analytik GmbH). We used the system to test the interferences of 8 VOCs (α- and β-pinene, Δ3-carene, limonene, linalool, trans-2-hexenylacetate, cis-3-hexen-1-ol, nonanol, toluene, and methanol). Additional experiments with β-caryophyllene and nonanol were unsuccessful because the volatility of these compounds was too low, i.e., the air concentration generated for these compoudns remained <50 ppb.

The Gasmet DX4015 analyser was used in the same way it was deployed for field measurements in previous studies: spectra were measured over 5 seconds and deconvoluted based on a library with 4 compounds (CH_4, H_2O, CO_2, N_2O). Measurements at all instruments were averaged over 10 sec intervals.

2.3 Laboratory tests 2 – Quantification of VOC interferences

In a second series of experiments, we aimed to quantitatively measure of VOC interferences. We modified the experimental setup such that VOC concentrations of the air passed to the CH_4 analysers could be controlled (Fig. 3b). VOC-free air and VOC carrying air were regulated separately by two mass flow controllers (MFC) (Bürkert GmbH) and mixed through a T-connector. The flow rate of VOC free air was kept constant at 1 L min^{-1} while the flow rate of the VOC carrying air was varied between 0 and 50 mL min^{-1}. The resulting flow rate, however, was too low to operate more than two instruments in parallel. We therefore alternated between three CH_4 analysers (Picarro G2301, LGR UGGA, GASMET DX 4040) while continuously monitoring the VOC concentrations with the PTR-MS. For this second series of experiments, we replaced the FTIR-based analyser with a newer model (GASMET DX4040) and increased the measurement cycle to one minute. The analyser was zero-calibrated with N_2 gas daily.

The PTR-MS was calibrated with a gas standard containing methanol, toluene, α-pinene (presenting also other monoterpenes: β-pinene, carene and limonene), cis-3-hexenol/hexanal as well as other VOCs not measured in this study. The concentrations of the other measured compounds were calculated based on the transmission curve obtained from the calibration (Taipale et al., 2008). Instruments were challenged with both step-wise changes and gradual increases of VOC concentrations (see Fig. 4), with 2-3 repetitions per instrument and test type. We tested six VOCs: β-pinene, δ3-carene, linalool, trans-2-hexenylacetate, cis-3-hexen-1-ol, and methanol.

2.4 Data analysis

FTIR spectra were deconvoluted using the software Calcmet to quantify the concentrations of methane and other trace gases. During Experiment 1, only CO_2, H_2O, CH_4 and N_2O were included in the spectra library. During experiment 2 and for the field measurements, we quantified the effect of adding a missing VOC to the spectral library. To do so, we analyzed the data twice, once with minimal library (CO_2, CO, N_2O, H_2O, NH_3) that did not contain the interfering VOCs, and once with spectra of VOCs in the library (additional compounds: methanol, a-pinene, b-pinene, carene, linalool, hexenol, nonanal, trans-2-hexenyl acetate, caryophyllene, limonene).

Interferences were calculated as the slope between VOC concentration and apparent CH_4 concentration. To avoid effects of transient interferences, we excluded time points where VOC concentrations abruptly changed (>35% change in VOC concentration per minute). Repeated challenges with the same test were combined in one regression analysis, but stepwise and gradual challenges were analysed separately. We calculated conservative estimates of uncertainty taking into consideration the uncertainty of the regression slope which already incorporates the variance among replicate tests. Our estimate of uncertainty furthermore accounts for minor variation in the CH_4 concentrations in the in-house pressurized air supply, which limited our ability to detect small interferences. We used a bootstrap approach to calculate this uncertainty. For this, the measured CH_4 concentrations were replaced those by a random period of the same length during when no experiments were conducted (i.e., air contained no VOC at this time and all observed variations in CH_4 concentrations represented true changes in CH_4 concentrations). This approach was repeated a total of 500 times. The 50^{th}, 97.5^{th}, and 2.5^{th} percentiles of the slope between these simulations was subtracted from the upper and lower limit of the confidence interval found in the regression analysis to obtain the central 95% confidence interval for the interference. Significance interference was assumed when these confidence intervals did not include zero.

FTIR measurements with libraries that included the tested VOCs also reported concentration for these VOCs. To evaluated the viability of measuring VOC concentrations by FTIR, we evaluated calculating the regression between VOC concentrations measured by FTIR and PTR-MS. We note that we made no attempts to calibrate FTIR based VOC concentration against external standards. All statistical analysis was conducted in the statistical programming environment R version 3.4.4 (R Development Core Team, 2015).

3 Results

3.1 Initial analysis of field data

Our initial field measurements showed a stark discrepancy between stem CH_4 emissions measured with the LGR UGGA and the GASMET DX4040 analysers. Measurements conducted with the LGR UGGA ranged from an apparent CH_4 uptake of -2 μg CH_4 h^{-1} m^{-2} and an apparent CH_4 emission of 7 μg h^{-1} m^{-2}. Measurements conducted with the DX4040 consistently showed an apparent CH_4 uptake ranging with a much larger flux (-145 to +8 μg CH_4 h^{-1} m^{-2}) (Fig 1). The average CH_4 fluxes were +0.44 ± 0.15 μg CH_4 h^{-1} m^{-2} (LGR UGGA) and -17.4 ± 3.7 μg CH_4 h^{-1} m^{-2} (GASMET DX4040).

3.2 Qualitative screening for interferences

An example for the changes in VOC concentrations over time produced by our setup is shown in Fig. 3a. The installation was first operated without a VOC present in the source to control for artefacts (e.g., effects of pressure changes due to switching valves). At the time point indicated by the vertical dashed line, a vial with β-pinene was inserted into the VOC source. This resulted in periodic patterns of presence and absence of β-pinene in the analysed air stream, with a maximum concentration of approximately 5 ppm.

The response of the CH_4 analyzers to the changing β-pinene concentrations is depicted in Fig. 3b-h. The FTIR-based analyser (DX4040) showed the strongest interference, with CH_4 readings reaching by up to 4ppm when β-pinene was added to the air stream, i.e., 2ppm above the actually CH_4 concentration (Fig. 3b). In contrast, measured CH_4 concentrations remained stable around 2ppm when setup was operated with an empty vial in the VOC source, demonstrating that the observed interferences were not artefacts produced by the experimental setup (i.e., pressure effects).

The Picarro G2301 analyser exhibited moderated interferences by *changes* in VOC concentrations (Fig. 3c). The sudden increase in the β-pinene concentrations resulted in temporary positive deviations corresponding to 20 ppb CH_4 ppm^{-1} β-pinene. We also detected a negative deviation when VOCs were suddenly removed from the air stream. A similar, but much weaker (1ppb) interference was also detected on the Picarro G2201i instrument (Fig. 3d). The LGR UGGA and the Picarro G4301 instruments showed no discernible effect of the addition of β-pinene was added to the air stream (Fig. 3e-f), however, for the G4301 analyser this was because relatively high noise and occasional [spikes?] in the measured CH_4 concentration may have masked potential small interferences. Finally, we did not detect any interference of β-pinene with the measured $\delta^{13}C_{CH4}$ values (Fig. 3g).

An overview of the interference tests with other VOCs is provided in Table 1. Among the 11 tested compounds, 9 showed an interference with the DX4015 analyser, 8 with the Picarro G2301, 6 with the Picarro G2201i, and 3 with the LGR UGGA. Interferences on the DX4015 were typically 2 orders of magnitude higher than on laser absorption based analysers. All interferences with CH_4 concentration measurements on the Picarro G2301 and G2201i instruments were transient, similar to those shown for β-pinene (Fig. 3c).

Only two VOCs interfered with $\delta^{13}C_{CH4}$ measurements by the Picarro G2201. First, toluene, which was added at high concentrations (30 000 -35 000 ppm) lead to an apparent increase in $\delta^{13}C_{CH4}$ values by 1‰. Second, an accidental addition of high concentrations of methanol (>80 000 ppb, likely higher due to saturation of the PTR-MS) strongly interfered with $\delta^{13}C_{CH4}$ measurements, leading to a positive deviation by about 900‰ with a memory effect that lasted more than 2 hours (not shown).

3.3 Quantification of interferences

In our second experiment, we successfully created gradual and stepwise changes in VOC concentrations. As an example, the effects of gradual and stepwise changes in $/beta$-pinene concentrations on the apparent CH_4 measured by three different analysers are shown in Fig. 4a-b and Fig. 4g-i, respoectively. In this experuiment, we did not detect a significant effect of β-pinene concentrations on CH_4 concentrations measured with the Picarro G2301 (Figs. 4c,4j) or the LGR UGGA instruments (Figs. 4f,4m). In contrast, β-pinene led to a significant underestimation of CH_4 concentrations with the Gasmet DX4040 (by approximately 120 ppb CH_4 ppm^{-1} β-pinene) when β-pinene and not part of the spectral library. Including β-pinene (and other VOCs in the spectra library significantly reduced this interference to approximately 1 ppb CH_4 ppm^{-1} β-pinene.

Similar results were found in tests with other VOCs. A list of the interferences quantified in different experiments is provided in Table 2. We did not detect a significant effect of VOC concentrations on the apparent CH_4 concentrations measured by the Picarro G2301 and the LGR UGGA. For β-pinene and 3-carene we constrained the upper confidence limits were <1 ppb CH_4 ppm^{-1} VOC on both instruments, for other compounds confidence limits were higher, mainly due to lower concentrations during the tests.

Interference on the Gasmet DX4040 without specific libraries for the tested compounds were high, ranging from -35 ppb ppm^{-1} (methanol) to 1800 ppb ppm^{-1} (cis-3-hexen-1-ol). Adding reference spectra of the tested VOCs to the library substantially decreased the interferences, but significant interferences weres still detected for β-pinene, 3-carene and hexenylacetate. (Table 2).

FTIR- and PTR-MS based measurements of VOC concentrations were highly correlated (R=0.956 to 0.998) for most compounds (Fig. 5). Poor correlations were found for linalool, which was present at concentrations close to or below the detection limit of the FTIR method (10 ppb).

3.4 Revised analysis of field data

After re-analysis with the full library, our field measurements by FTIR showed smaller CH_4 fluxes than in our initial analysis (Fig. 1). The methane emission rates generated in this revised analysis (-85 to +8 μg CH_4 h^{-1} m^{-2}), however, still showed a substancial net uptake of CH_4. The average apparent CH_4 flux was -10.1 ± 1.6 μg CH_4 h^{-1} m^{-2}. Assuming that measurements conducted by OA-ICOS revealed the true CH_4 flux, the re-analysis decreased the bias in FTIR based measurements by 41%.

4 Discussion

4.1 FTIR-based analysers

Our results show that FTIR-based gas analysers are vulnerable to interferences from co-emitted VOCs. Measurements of plant CH_4 emissions with enclosure chambers by this principle can result in gross over- or under-estimations of the actual CH_4 flux rates depending on the combination of co-emitted VOCs as well as the components included in the spectral library used to deconvolute the measured spectra. Had we solely relied on FTIR to quantify CH_4 fluxes during our field campaign in Skogaryd, we would have identified spruce stems as a strong sink of CH_4 (Fig. 1). However, concurrent measurements by the OA-ICOS-based LGR UGGA, which were largely unaffected by VOC co-emissions (Table 2), revealed that these trees stems actually act as a small source of CH_4. The comparison of OA-ICOS- and FTIR- based results indicates that tree stem VOC emissions at Skogaryd were dominated by compounds that negatively interfere with FTIR measurements CH_4 measurements, including methanol, β-pinene, and hexenylacetate. The effect of these VOCs outweighted the positive interference of other VOCs including Δ3-carene and hexenol. It is, however, important to note that we did not quantify the interfereces of all potential VOCs, including the dominant compound emitted by spruce trees (α-pinene) (Grabmer et al., 2006; Janson, 1993).

Our second experiment further showed that the VOC interferences can be minimized by including all potentially occurring VOCs in the spectral library. In our experiments, this decreased the interference by 1-2 orders of magnitude 2. This, however, may not be practical in many field settings, where the identity of VOCs released from plants and soils is often unknown. Furthermore, spectral deconvolution was not successful for all VOCs, and significant interferences were found for three of the tested VOCs (β-pinene, Δ3-Carene, and hexenyl acetate) even when the reference spectra were present in the spectral library. Upper limits for the quantified interferences in FTIR-based measurements were typically an order of magnitude higher than on laser absorption based instruments. In the case of our field campaign in Skogaryd, on average 59% of the interference persisted when data were re-analysis with additional spectra in the library (Fig. 1).

Our study, however, also showed that FTIR analysis may be a useful method to study VOC fluxes instead of or in addition to PTR-MS measurements. The strong correlation between VOC concentrations quantified by FTIR and PTR-MS (Fig 5) indicates that FTIR can conduct precise measurements of VOC concentrations. FTIR instruments are cheaper and more portable than PTR-MS instruments and provide a complementary analytical principle that could help distinguish between isomers that cannot be separated by mass spectrometry. Detection limits of FTIR based measurements of VOC concentrations (10s of ppb), however, are substantially higher than those of PTR-MS based measurements (10s of ppt), and cross sensitivities among VOCs may bias the quantification of compounds that occur at lower concentrations.

4.2 Laser spectroscopy based analysers

Interferences on the CRDS- and OA-ICOS- based systems were significantly lower than on FTIR-based systems, but during our qualitative screening we still detected some potentially important interferences (Fig. 3), especially the case for the Picarro G2301. On this analyser, sudden changes in VOC concentrations resulted in minor deviations of the measured CH_4 concentration. These interferences, however, were corrected by the instrument over the course of approximately 30 sec and are therefore unlikely to affect chamber measurements, where concentrations of VOCs and CH_4 increase gradually (e.g., over a 20–40 minutes chamber closure).

These interferences may, however, pose an important bias for measurements that rely on fast measurements of air masses with changing VOC concentrations, as used for Eddy covariance (EC) measurements. In these measurements, interferences from VOC emissions as detected in this study could lead to an overestimation of CH_4 emissions. We have, however, not been able to further investigate VOC interferences on the high-frequency analysers used for EC measurements.

5 Conclusions

We quantified the interference of VOCs on CH_4 analysers based on FTIR and laser absorption spectroscopy. FTIR based instruments were more prone to higher levels of interference than laser absorption based instruments, even when VOCs were added to the spectral library. We therefore recommend to avoid the use of FTIR based trace gas analysers in applications were high fluxes of VOCs relative to the target gas are expected, as is the case for chamber measurements of plant and forest floor CH_4 fluxes. Our results, however, indicate that using the correct spectrum libraries, FTIR instruments can be a cost-effective solution to field measurements of certain VOCs.

Code and data availability. Raw data, processed data, and code are available at doi:10.5281/zenodo.2597716.

Author contributions. LK had the main responsibility for analysing the data and writing the manuscript; and participated in the designing and construction of the measurement setup. MK had the main responsibility for designing the measurement setup and programming the controlling software; and participated in constructing the measurement setup and in the writing process. KR had the main responsibility for the VOC measurements and processing of PTR-MS results. IH had the main responsibility for the field campaign and had the original idea for testing the interference of VOCs in CH_4 analysers; and participated in designing the measurement setup. TP had the main responsibility for constructing the measurement setup; and participated in designing the measurement setup. HH contributed to the conceptualisation of the study and was responsible for deciding and providing the measured VOCs. MP contributed to the conceptualisation of the study and the writing of the manuscript.

Competing interests. The authors declare no conflict of interest.

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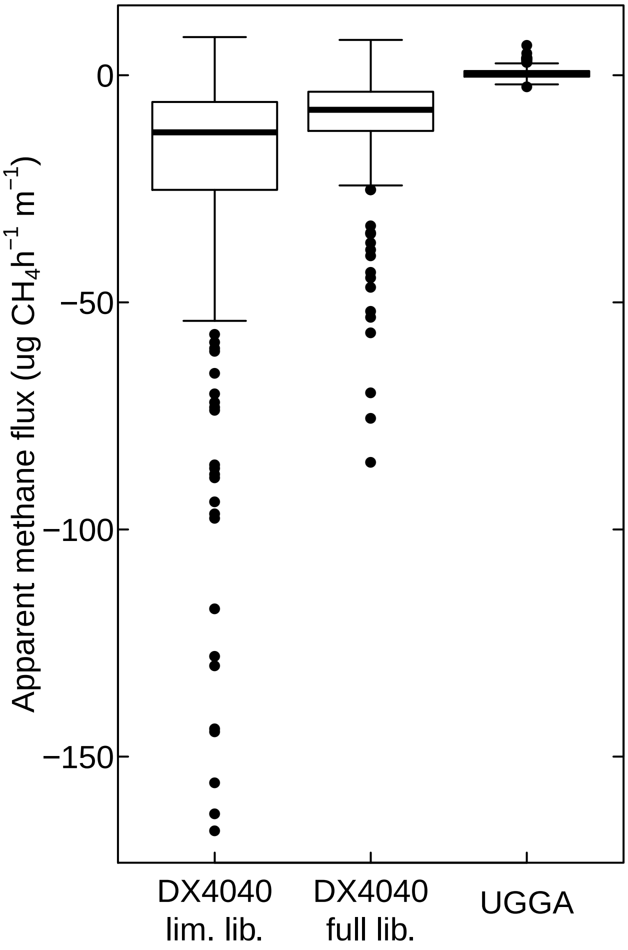

Figure 1. Apparent tree stem methane fluxes when quantified with a laser spectroscopy based analyser (LGR UGGA) and a FTIR based analyser (Gasmet DX4040). FTIR based fluxes are shown calculated based on spectral deconvolution with a minimal library that did not contain VOC spectra (min. lib.), and with a library that contained spectra of commonly occurring VOCs (full lib.).

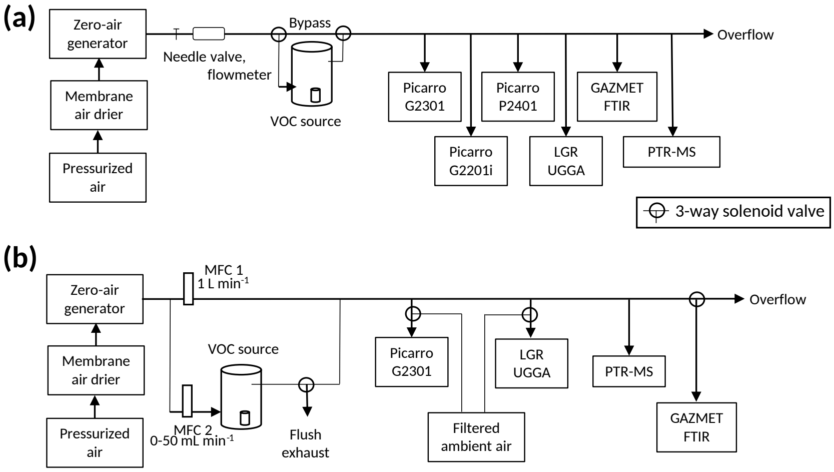

Figure 2. Schematic for air flow in laboratory test 1 (panel **a**) and 2 (panel **b**).

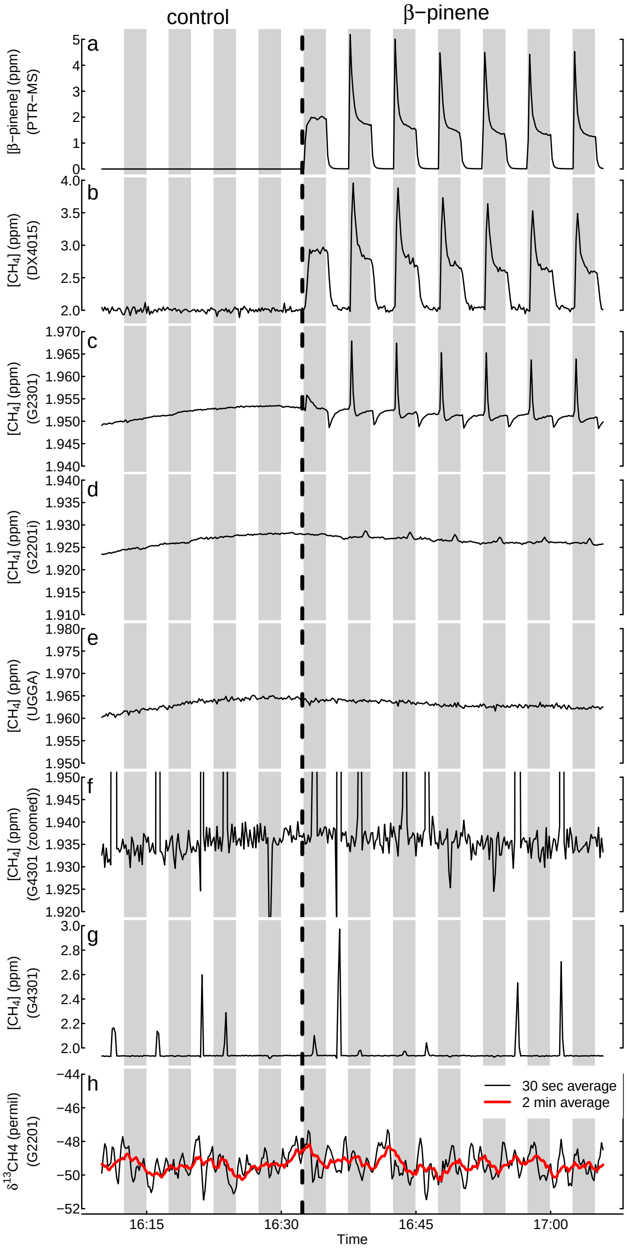

Figure 3. Development of VOC (panel **a**) concentration as measured by PTR-MS and apparent CH_4 concentration as measured by Gasmet DX4015, Picarro G2301, Picarro G2201i, LGR UGGA and Picarro G4301 (panels **b–g**, respectively) and δ^{13}C-CH_4 values as measured by Picarro G2201i (panel **h**). White areas indicate the times when the system was set to bypass the VOC source, grey shaded areas times when the VOC source was online. During the control period left of the dashed vertical line the VOC source was empty. At the position of the dashed vertical line, β-pinene vial was introduced into the standard source. Black line represents 10-second moving average of apparent CH_4 concentrations and $\delta^{13}C_{CH4}$ values, red thick line 30-second moving average of appearent $\delta^{13}C_{CH4}$ values. Notice G4401 results zoomed in panel **f** to visualise background variation; full-scale results in panel **g**.

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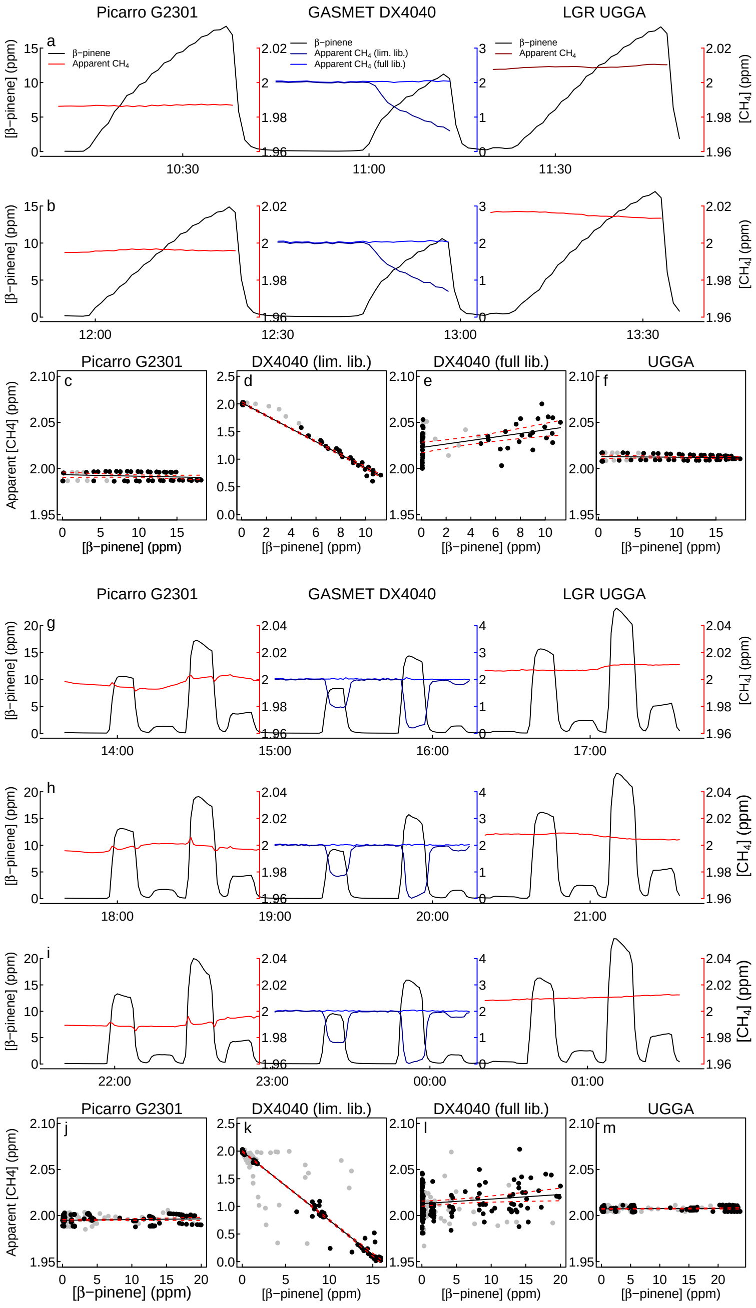

Figure 4. Quantitative measurements of the effect of β-pinene concentrations on the measured (apparent) methane concentration when analysers were challenged with a gradual increase (**a-f**) or stepwise changes in β-pinene concentrations (**g-i**). The figure depicts both the time course of β-pinene and apparent CH_4 concentrations (**a-b**; **g-h**) and the relationship between β-pinene and the measured CH_4 concentration (**c-f**; **i-l**). Black lines in panels c-f and i-l indicate linear regressions, dashed red lines the 95% confidence interval of these regressions. Data points that occurred after after a rapid changes in the β-pinene concentration and that were therefore excluded from the regression analysis are depicted in grey.

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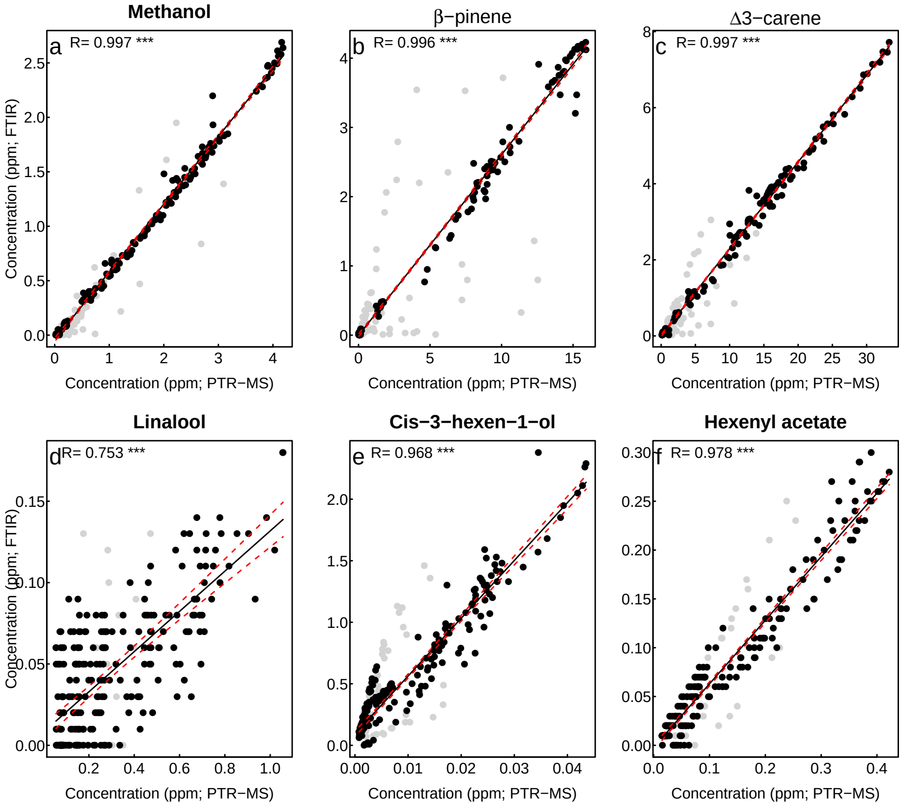

Figure 5. Correlation between FTIR- and PTR-MS based measurements of VOC concentrations. Data points plotted in grey were excluded after rapid changes in VOC concentrations. Asterisks indicate significante levels: *, $p<0.05$; **, $p<0.01$; ***, $p<0.001$.

Table 1. Summary of interferences detected in qualitative tests

Compound		Interference (ppb apparent CH4)				
name	conc. range (ppb)[ion]	Gasmet DX4015	Picarro G2301	Picarro G2201i	Picarro G4301	LGR UGGA
Methanol	6 000 - 10 000 [33]	500 - 700	15[a]	2[a]	–	2
α-pinene	4 000 - 5 000 [137]	1 500 – 2 000	10-15[a]	1[a]	–	–
β-pinene	5 000 - 15 000 [137]	2 000	5-30[a]	1[a]	–	–
Carene	3 000 - 7 000 [137]	7 000 - 12 000	–	–	–	
R(+)limonene	900 - 1 100 [137]	400 - 500	5[a]	–	–	–
Linalool	7 000 – 12 000 [155]	300 - 600	8-25[a]	3-8[a]	–	0-8
Cis-3-hexen-1-ol	20-60 [101]	600 – 3 000	10-15[a]	–	–	–
Trans-2-hexenyl acetate	500 – 2 000 [143]	600 - 2 600	10-50[a]	2-12[a]	–	–
Toluene	30 000 – 35 000 [93]	5 000 – 10 000	200-250[a]	15-20[a]	–	2

–, not detected

[a] Transient interference triggered by change in VOC concentrations rather that presence of VOC

Table 2. Quantified interferences of volatile organic compounds on CH_4 analysers. Significant interferences are indicated indicated in bold.

		Interference (ppb apparent CH4 per ppm VOC; 95% CI)			
		Picarro G2301	LGR UGGA	Gasmet DX 4040 w/ lib	Gasmet DX 4040 w/o lib
Methanol	stepwise	0.37	0.25	3.49	**-35.8**
		(-2.69 - 3.77)	(-3.25 - 3.33)	(-1.06 - 8.02)	**(-40.4 - -31.3)**
	gradual	3.88	1.33	2.66	**-36.6**
		(-7.76 - 9.71)	(-5.91 - 6.36)	(-9.37 - 10.7)	**(-48.6 - -28.6)**
β-pinene	stepwise	0.15	0.05	**0.70**	**-123.8**
		(-0.28 - 0.64)	(-0.29 - 0.41)	**(0.01 - 1.73)**	**(-125.5 - -122.0)**
	gradual	-0.12	-0.06	1.94	**-118**
		(-1.82 - 0.74)	(-1.28 - 0.82)	(-0.12 - 3.41)	**(-122 - -114)**
Δ3-Carene	stepwise	0.22	0.10	**4.23**	**64.8**
		(-0.65 - 0.77)	(-0.64 - 0.78)	**(3.15 - 5.13)**	**(63.4 - 65.9)**
	gradual	-0.18	-0.16	**3.40**	**63.2**
		(-1.28 - 0.53)	(-1.27 - 0.51)	**(2.04 - 4.34)**	**(61.3 – 64.6)**
Linalool	stepwise	2.26	-1.12	17.4	-12.0
		(-15.1 - 18.0)	(-16.1 - 13.7)	(-7.80 - 40.3)	(-36.1 - 9.88)
	gradual	19.8	-0.16	17.7	-14.8
		(-17.8 - 79.4)	(-33.2 - 20.7)	(-26.0 - 65.9)	(-58.3 - 33.6)
Cis-3-hexe-1-nol	stepwise	4.80	-5.81	477	**1800**
		(-431 - 229)	(-387 - 275)	(-105 - 903)	**(1230 – 2210)**
	gradual	36.3	15.6	646	**2210**
		(-692 - 277)	(-802 - 516)	(-350 - 1240)	**(1210 - 2810)**
Trans-2-hexenyl acetate	stepwise	1.39	1.94	**-42.6**	**-402**
		(-15.1 - 21.3)	(-17.8 - 22.6)	**(-74.9 - -8.16)**	**(-439 - -362.4)**
	gradual	1.95	2.83	**-126**	**-742**
		(-25.5 - 37.3)	(-40.8 - 34.2)	**(-190 - -63.8)**	**(-820 - -667)**