Dear Dr. Niemann, Dear Reviewers,

Please find attached our revised manuscript "Technical note: Interferences of volatile organic compounds (VOC) on methane concentration measurements". We thank the two reviewers for their constructive feedback, which has helped to further improve the manuscript. Please see below our detailed response to each of the reviewers' comments.

Both reviewers suggested that the manuscript should clarify whether the VOC mixing ratios applied in our experiment are representative for actual chamber measurements. In the revised manuscript, we now present estimates for the VOC mixing ratios expected at the end of soil, stem, and shoot chamber closures along with estimates of the bias VOC interferences excert over CH4 flux measurements in these chambers. While these estimates rely heavily on assumptions and simplifications, we hope that they provide the reader with a better understanding for where relevant VOC interferences are to be expected and what order of magnitude they can reach in different ecosystem compartments.

All other comments were addressed to meet the reviewers' recommendations. Given the short length of the technical note, we were unable to incorporate answers to all of the reviewers' technical questions in the manuscript itself, instead we provide answers to some of the reviewers' questions this (public) response letter.

Yours sincerely,

Lukas Kohl (on behalf of all co-authors)

Detailed response to reviewer comments

(*reviewer comments in italic,* our response in normal font. We abbreviate page and line numbers such that p2 L15 refers to page 2 line 15. We apologize for inconveniences caused by line numbers restarting with every new page which, unfortunately, is set by the Biogeosciences LaTeX template)

Editor's comments:

*Dear Lukas Kohl and co-authors,*

*two anonymous reviewers evaluated your MS and both seem quite positive about your work. I found your replies good, too and would this like to prepare a revised version of your MS for consideration after minor revisions. Please note that a new MS file needs to be uploaded (I noted that you uploaded your revised MS as an author comment in the discussion, and thought the revised version seems fine for the most part, note that it needs to be uploaded separately).*

*In addition to the reviewer comments, I would like you to clarify in the MS if differential material is used (ie standard alpha pinene).*

I assume that this refers our response to R2.5 ("Unfortunately, we ran out of our α-pinene standard during experiment 2 and therefore used β-pinene and Δ3-carene to represent monoterpenes").

For clarification, we tested three monoterpenes in experiment 1 (α-pinene β-pinene, and Δ3-carene), and two monoterpenes in experiment 2 (β-pinene and Δ3-carene). In our response we explain why we chose these two monoterpenes for experiment 2 and left out α-pinene (we ran out of the standard). We did not want to imply that any standard was changed between the experiments. This should be clear from p3 L29-30 and p4 L18-19.

*Also make sure that figures are well readable. While I found fig 3 easy to interpret, figs 4 and 5 are composed of rather thin lines , the colour scheme of which gets difficult to see, particularly if these are furhter shrunk.*

We increased the line width and legend font size and added different line weights to make it easier to discriminate between the lines. I hope the figure is easier to read now – please let us know if further changes to this figure are required.

*It is also not clear to me why the apparent methane concentrations of the different instruments are plotted on different scales.*

The different scales are due to the vast differences in instrument precision and detected interferences. For the LGR and Picarro instruments, we want to highlight that the measured $CH_4$ mixing ratios are constant with very high precision (on the scale of single ppb). For FTIR with the limited library, we want to show that the measured $CH_4$ mixing ratios vary on the scale of ppm, and that these variations follow the same pattern as the β-pinene concentrations. Finally, we want to show that these interferences are minimized when FTIR data is analysed with a complete spectral library.

Reviewer 1:

*General comments*

*The paper by Kohl et al. describes cross sensitivities of several volatile organic compounds on methane measurements when using different optical analysers. I consider the results of the paper of major interest to all those monitoring methane fluxes in the field or laboratory from ecosystems and biological systems that are known to release VOC at substantial amounts. I found the manuscript to be well written and structured.The results are clearly presented and discussed in a straightforward manner, providing the scientific community with important information about how emissions of VOC released from the biosphere might interfere with measurements of methane when using state of the art optical measurement systems. I recommend publication of the manuscript as a Technical Note in Biogeosciences after minor revisions. I have only a few comments which I hope the authors might consider in their revised manuscript.*

R1.1: *I would suggest using ppmv/ppbv/pptv (parts per million/billion/trillion by volume) throughout the whole manuscript instead of ppm/ppb/ppt.*

**Changed throughout the manuscript.**

R1.2 *Furthermore, the correct expression for ppmv would be mole fraction. However, I also understand if the authors would like to keep the more commonly used term "concentration".*

**Changed to 'mixing ratio' throughout the manuscript.** We kept the more commonly used term 'concentration' in the title.

R1.3 *As water vapour might substantially affect measurements of methane (both concentrations and stable carbon isotopes) when using optical analyzers I would suggest to add a few sentences how the authors have dealt with this issue during their investigations in the field and in the laboratory.*

Laboratory measurements: Water was removed from the pressurized air used for the laboratory experiments (SMC membrane dryier) and water contents remained <0.2% absolute humidity throughout the experiment. Water vapour therefore did not affect $CH_4$ concentration or stable carbon isotope measurements.

Field measurements: Both analysers quantified water concentrations and used these concentrations to corrected $CH_4$ concentrations. No carbon isotope values were measured during the field measurements reported in this manuscript.

R1.4 *Please add some information what are typical emission rates of some VOC released from vegetation/trees in the field and put them into relation with the amounts that have been applied in the laboratory study.*

**Changed as requested.** Thanks for this suggestion; we think that this adding such information strengthened the paper a lot. Typical VOC emission rates and estimates for mixing ratios reached during chamber closures are now provided in the new Tables 1 and 4. Overall, the mixing ratios employed in our experiment are above those likely to occur in soils and stem chambers, but below those likely found in shoot chambers.

R1.5 *Figure 4: There are too many subfigures included and for some subfigures it is rather difficult to decipher the information. Please revise and split into two or three figures to increase readability.*

**Changed as requested.** We removed three panels and split Fig. 4 two figures (new Figs. 4 and 5)

*Technical corrections*

R1.6 *Page 5, line 6, Results: add CH4 after 7µg...*

**Changed** (p5 L9).

R1.7 *Page 5, line 25, Results: something is wrong with this sentence, revise*

**Changed** (p5 L29).

R1.8 *Page 6, line 23: change "weres" to "were"*

**Changed** (p6 L29).

Reviewer 2

*Review of: "Interferences of volatile organic compounds (VOC )on methane concentration measurements" by Kohl et al.*

*The paper studies experimentally the interferences of several VOCs on the measurement results of several CH4 analysers. VOCs interfere strongly with FTIR but not with laser absorption spectroscopy measurements of CH4. The results indicate that the FTIR instruments are not suitable for CH4 measurements in high-VOC conditions, e.g. when estimating CH4 fluxes from plants or soil. Laser absorption spectrometers are much less affected by VOC interference, thus can be used in high-VOC conditions. Including the main VOCs in the FTIR library corrects for part but not all the interference on methane. A by-product of this study is the finding that VOCs can be quantified by FTIR, at least at the high concentrations used here.*

*The paper is very useful given the recent increase in attention to CH4 emissions from or via trees, and the increasing availability of field capable instruments. The paper is well written and I recommend publication after the comments below are addressed.*

*General comments*

R2.1 *I think it is important to discuss the relevance of these findings for the recent studies of methane emissions form trees (e.g. summarized in Covey et al., 2019). Did any of these studies use FTIR instruments?*

We are unaware of any published tree $CH_4$ flux data that used FTIR based instruments. Many of the studies summarized by Covey et al us gas chromatography to quantify $CH_4$ (which is not vulnerable to the interferences described herein), while some of the more recent studies quantified $CH_4$ by laser spectroscopy (Picarro and LGR instruments). We are, however, aware of several groups currently considering the use of FTIR instruments for stem flux measurements. We therefore think that the reliability of currently available data is not impacted by our work, but that this manuscript is important as the potential use of FTIR for tree stem flux measurements would decrease this data reliability in the future.

R2.2 *"Concentration" is not the correct term for molar ratios (i.e. all the quantities expressed as ppm or ppb). "Mole fraction" or "mixing ratio" should be used instead.*

**Changed to 'mixing ratio' throughout the manuscript.** We kept the more commonly used term 'concentration' in the title.

R2.3 *An explanation is missing on how the VOCs to be tested were chosen. Are these representative for real world emissions from vegetation?*

**Clarified as requested.** p3 L3-5 now read "We chose the tested compounds to represent a cross-section of naturally occurring VOCs and aimed to cover different chemical compound classes rather than the most important biogenic VOCs occurring in any given environment."

R2.4 *The VOC concentrations used in the lab experiments seem quite high. Are these representative for what one can expect in a tree chamber? Consider mentioning this in the method already. Also, when discussing the sensitivities of CH4 to VOCs, it would be useful to relate to real world expected VOC levels.*

**See response to R1.4.** We added the new Sections 2.5 and 3.5, Fig. 7, and Tables 1 and 4 to provide estimates for VOC mixing ratios reached during chamber closures.

R2.5 *not all VOCs from Test 1 were used in Test 2 –why? Did the ones that were removed not have an influence? Especially alpha-pinene, which the authors mention it is the main VOC emitted by spruce.*

Due to time constraints and limited instrument availability. While the tests conducted during Experiment 1 took around 1h per compound, tests in Experiment 2 took one overnight run per compound. We chose the VOCs tested to cover a broad diversity of chemical compound classes (monmoterpenes, methanol, aliphatic and aromatic compounds). Unfortunately, we ran out of our alpha-pinene standard during experiment 2 and therefore used β-pinene and Δ3-carene to represent monoterpenes.

R2.6 *two different FTIR instruments were used, one in the field campaign and Test 2, and the other one in Test 1. Are these similar enough that the results can be considered together? If yes, please state in the text. Otherwise they should probably be treated separately through the paper.*

**Clarified as requested.** These are very similar instruments (DX4040 is the portable version of DX4015). They have the same measurement cell, detector technology, and spectral deconvolution software. p4 L16-18 now read "[...] we replaced the FTIR-based analyser with a portable but otherwise similar model [...]"

*Specific comments*

R2.7 *at the end of Introduction the authors state that the test setup was built. I suggest adding one sentence stating clearly what is presented in this paper: the field experiments? or the lab test setup? the results of both?*

**Modified as requested.** We added the following sentence at the end of the introduction "In this communication, we present results from field measurements and laboratory tests, as well as a first sensitivity analysis for the impact of VOC interferences on measurements of $CH_4$ fluxes from different ecosystem compartments." (p2 L28-30)

R2.8 *page 2 lines 14-19: the phrase is a bit long and hard to follow, with some commas missing. Please consider reformulating.*

**Modified as requested.** p2 L19-21 now read "This is especially important in the study $CH_4$ emissions by plants as plants co-emit a complex mixture of volatile organic compounds (VOC) at fluxes 2 to 4 orders of magnitude higher than currently reported $CH_4$ fluxes [references]."

R2.9 *page 3 lines 6-7: specify what the in house pressured air supply is based on: e.g. gas cylinder(s) or a large compressor taking outside air. This is relevant for how the uncertainty is calculated (page 4, and see comment below)*

**Clarified as requested.** The air was taken from a compressor using outside air. (p3 L18)

R2.10 *page 3 line 21 and page 4 line 9: are δ3-carene and Δ3 -carene the same chemical?*

**Corrected.** This should be a uppercase delta in all cases. (p4 L23)

R2.11 *Fig. 3: Caption –specify the experiment these data come from. For panel a, the text says "development of VOC concentration" but only beta-pinene is shown.*

**Changed as requested.** The caption to Fig 3. now starts "Exemplary results from Experiment 1, shown for tests conducted with β-pinene."

R2.12 *page 4 lines 22-30: if the in house supply of pressured air takes atmospheric air from outside, there will be non-random variations on diurnal time scales, with e.g. possibly large methane increase during night. Is this taken into account in the bootstrap, i.e. are the 500 time intervals from the same part of day as the VOC experiments? Or was the day/night variation in the inhouse air estimated?*

The data used for bootstrapping was collected during nighttime (7pm to 7am). Experiment 2 runs were started between 10am and 4pm and ran until 1am to 8am. This means that there is indeed a small potential that we underestimated non-random variations in CH4 concentrations that occurred during daytime. This affects mainly gradient challenges, which were conducted before the stepwise challanges in the same run.

The bootstrapping approach was employed to account for the added uncertainty due to drifts in the inlet $CH_4$ mixing ratio. These additional uncertainties were largely symmetrical, which suggests that periods of increasing and decreasing $CH_4$ concentrations were equally represented in the data used for bootstrapping. We conducted every individual challenge (VOC / analysers / stepwise-or-gradient combination) at least twice, with >1.5h (gradients) or >4h (stepwise) between measurement. Overall, we think that in spite of diurnal variations estimates still represent a fairly conservative estimate for the true uncertainty in our experiments.

R2.13 *Fig. 4: I find some parts of Fig. 4 confusing. In panels a and b it is not easy to understand which trace corresponds to which y-axis. E.g., in the upper middle panel, do the methane data correspond to the blue unlabeled scale, or to the side scales labelled "CH4"? What does the blue y-*

*axix represent, and what are the units? Consider splitting the panels. Similar for panels g, h, i.Also, please consider splitting Fig 4 into two figures.*

**Changed as requested.** We split Fig 4 into two separate figures (new Figs. 4 and 5), removed three panels, and revised the corresponding figure captions.

R2.14 *page 5 Sect 3.1: suggest to refer to Fig 1.*

**Changed as requested.** We moved the reference to Fig 1 up by one sentence to meet the first mention of data from Fig. 1 in this paragraph (p6 L9).

R2.15 *page 7 line 13: was alpha-pinene not included in Test 1?*

No. While we did screened for (and detected) interferences by α-pinene in experiment 1, but we did not conduct <u>quantitative</u> measurements of α-pinene interferences (hence, we note that they were not quantified.)

*Text comments:*

R2.16 *page 1, line 7: typo"strong strong"*

**Corrected** (p1 L9).

R2.17 *page 2 line 29: typo "Summer"*

**Corrected.** (p2 L4).

R2.18 *page 3 line 6: "Fig 3a" –should it also be "Fig 2a", since this is the setup decription?*

**Corrected** (p3 L17).

R2.19 *page 3 lines 9-10: "The flowair" –should it be "the air"?*

**Corrected** (p3 L21).

R2.20 *page 3 line 29: "measure of VOC interferences" should be "measure the VOC interferences"?*

**Changed to "measure VOC interferences".** (p4 L10)

R2.21 *page 3 line 30:"Fig 3b" –should it be "Fig 2b"?*

**Corrected** (p4 L11).

R2.22 *page 4 line 25: "those by a random period" should be "by those from a random period"*

**Corrected** (p5 L10).

R2.23 *please check-page 4 line 29: "Significance interference" should probably be "Significant interference"*

**Corrected** (p5 L 14).


R2.24 *page 4 line 31: "to evaluate"-page 4 line 32: "we evaluated calculating" should be "we calculated" ?*

**Corrected** (p5 L17).


R2.25 *page 5 line 26: probably typo: [spikes?]*

**Corrected to 'outliers'.** (p6 L30)


R2.26 *page 6 line 10: typo "/beta"*

**Corrected** (p7 L15).


R2.27 *page 6 line 14: I think "and not part of ..." should be "was not part of ..."*

**Corrected** (p7 L 19).


R2.28 *page 6 line 15: ")" missing after "VOCs"*

**Corrected** (p7 L20).

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

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**Abstract.** Studies that quantify plant methane (~~$CH_4$~~$CH_4$) emission rely on the accurate measurement of small changes ~~$CH_4$ concentrations~~ in the mixing ratio of $CH_4$ that coincide with much larger changes in the ~~concentration~~ mixing ratio of volatile organic compounds (VOCs). Here, we assessed if 11 commonly occurring VOCs (e.g., methanol, $\alpha$- and $\beta$-pinene, $\Delta$3-carene) interfered with ~~$CH_4$ concentrations measurements~~ the quantitation of $CH_4$ by five laser absorption spectroscopy and Fourier-transformed infrared spectroscopy (FTIR) based ~~$CH_4$~~ $CH_4$ 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~~ based analysers, and underlined the importance of identifying and compensating for interferences with FTIR instruments. When VOCs were not included in the spectral library, they exerted a strong ~~strong~~ bias on FTIR-based instruments (64 - 1800 ~~ppb apparent $CH_4$~~ ppbv apparent $CH_4$ / ~~ppm VOC)bias on FTIR based measurements, which can lead to substantial over- and underestimations of $CH_4$ fluxes~~ppmv VOC). Minor (0.7 - 126 ~~ppb~~ ppbv / ~~ppm)~~ ppmv) 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~~ ppbv / ~~ppm)~~ ppmv) and transient (<1 minute) VOC interferences on laser absorption spectroscopy based analysers. ~~Our results thus suggest that FTIR~~ Overall, our results demonstrate that VOC interferences have only minor effects on $CH_4$ flux measurements in soil chambers, but may severely impact stem and shoot flux measurements. Laser absorption based instruments are ~~not well suited for quantifying plant $CH_4$ emissions. However, our results also suggest~~ better suited to for quantifying $CH_4$ fluxes from plant leaves and stems than FTIR based instruments, significant interferences in shoot chamber measurements could not be excluded for any of the tested instruments. Our results furthermore showed that FTIR can precisely quantify VOC ~~concentrations~~mixing ratios , and could therefore provide a method complementary to proton-transfer-reaction mass spectrometry (PTR-MS).

1

# 1 Introduction

Gas analysers based on infrared spectroscopy are increasingly used to study fluxes of ~~CH₄~~ 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 cur-

5  rently considered state of the art by international flux stations networks (Franz et al., 2018). These analysers quantify trace gas ~~concentrations~~ mixing ratio through absorption at one specific wavelength. Fourier-transformed infrared spectroscopy (FTIR) is another approach to measure ~~greenhouse~~ trace 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)~~ analytes (e.g. Warlo et al., 2018; Teutscherova et al., 2019; Kandel et al., 2018; Jurasinski et al., 2019). FTIR based analysers

10  measure a complete infrared absorption spectrum, and then quantify the ~~concentrations~~ mixing ratio 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).

15  Plants were recently identified as an important component of the natural cycles of ~~CH₄~~ 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~~ CH$_4$ 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 ~~CH₄~~ 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 ~~CH₄ concentrations~~

20  the mixing ratio of CH$_4$ over time are monitored (Covey and Megonigal, 2019). This monitoring of ~~CH₄ concentrations~~ CH$_4$ mixing ratios 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 ~~CH₄ concentrations~~ CH$_4$ mixing ratios 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

25  of ~~CH₄~~ CH$_4$ fluxes, but have also increased vulnerability towards mismeasurements due to spectral interferences. This is especially important in the study ~~CH₄~~ CH$_4$ emissions by plants as plants co-emit a ~~variety~~ complex mixture of volatile organic compounds (VOC) ~~along with CH₄ which have a high potential to interfere with CH₄ analysis given that these VOC can be emitted at rates~~ at fluxes 2 to 4 orders of magnitude higher than currently reported ~~CH₄~~ CH$_4$ fluxes (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

30  interfere with ~~CH₄ concentration~~ CH$_4$ mixing ratio measurements, however, has so far not been evaluated.

In a recent field campaign, we conducted parallel measurements of tree stem ~~CH₄~~ CH$_4$ emissions with two distinct methane analysers (Los Gatos Research (LGR) UGGA and GASMET DX4040). The two analysers gave contradicting results, with apparent ~~CH₄~~ CH$_4$ fluxes differing both in direction and in magnitude (Fig 1). We ~~hypothesized~~ hypothesised that these divergent measurements resulted from interferences of VOCs with ~~CH₄~~ 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. In this communication, we present results from field measurements and laboratory tests, as well as a first sensitivity analysis for the impact of VOC interferences on measurements of CH$_4$ fluxes from different ecosystem compartments.

## 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 spruce 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 analysers, a Los Gatos Research (LGR) UGGA CH$_4$/CO$_2$/H$_2$O analyser and a Gasmet DX4040 FTIR based multi-compound analyser. CH$_4$ exchange rates were quantified as the increase in CH$_4$ mixing ratio 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 2nd to 13th and from July 25th to August 5th 2018, alternating between the two instruments. In addition, we measured soil CH$_4$ fluxes from 9 soil collars (0.26 m$^2$) using a static chamber technique described previously (Klemedtsson et al., 2010). Measurements were conducted daily between June 2nd and 13th, again alternating between the LGR UGGA and Gasmet DX4040 analysers.

### 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 an air stream with a constant CH$_4$ mixing ratio (Fig. 2a). Air from the in-house pressured air supply (compressed outdoor air) 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 the air used for our experiments contained atmospheric CH$_4$ at atmospheric mixing ratios. The 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 that contained a pure VOC standard placed 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$^{-1}$~~min$^{\prime\prime-1\prime\prime}$). We tested four analysers based on laser spectroscopy (CRDS), including two stationary instruments (Picarro G2301 ($CO_2$, ~~CH$_4$~~$CH_4$, $H_2O$); Picarro G2201i ($^{13}CO_2$, ~~$^{13}$CH$_4$~~$^{13}CH_4$, $H_2O$) and two portable instruments (Picarro G4301; LGR UGGA ($CO_2$, ~~CH$_4$~~$CH_4$, $H_2O$)), as well as ~~one analyser based on~~ a Fourier-transformed infrared (FTIR) spectroscopy based multi-compound analyser (GASMET DX4015). For control, we quantified VOC concentrations ~~by~~ with a proton transfer reaction quadrupole mass ~~spectrometry~~ spectrometer (PTR-MS, Ionicon Analytik GmbH). We used the system to test the interferences of 8 VOCs ($\alpha$- and $\beta$-pinene, $\Delta$3-carene, limonene, linalool, trans-2-hexenylacetate, cis-3-hexen-1-ol, nonanol, toluene, and methanol). Additional experiments with $\beta$-caryophyllene and nonanol were unsuccessful because the volatility of these compounds was too low, i.e., the ~~air concentration~~ mixing ratios generated for these ~~compoudns~~ compounds remained <50 ~~ppb.~~ ppbv. We chose the tested VOCs to represent a cross-section of naturally occurring VOCs and aimed to cover a wide range of chemical compound classes rather than the most important biogenic VOCs occurring in any given environment.

The Gasmet DX4015 analyser was used in the same way it was deployed for ~~field~~ soil flux measurements in previous studies: spectra were measured over 5 seconds and deconvoluted based on a library with 4 compounds (~~CH$_4$~~$CH_4$, $H_2O$, $CO_2$, $N_2O$). 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~~ mixing ratios of the air passed to the ~~CH$_4$~~$CH_4$ analysers could be controlled (Fig. ~~3~~2b). 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$^{-1}$~~min$^{-1}$ while the flow rate of the VOC carrying air was varied between 0 and 50 mL ~~min$^{-1}$~~min$^{\prime\prime-1\prime\prime}$. The resulting flow rate, however, was too low to operate more than two instruments in parallel. We therefore alternated between three ~~CH$_4$~~$CH_4$ analysers (Picarro G2301, LGR UGGA, GASMET DX 4040) while continuously monitoring the VOC ~~concentrations~~ mixing ratios with the PTR-MS. For this second series of experiments, we replaced the FTIR-based analyser with a ~~newer~~ portable but otherwise similar 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, $\alpha$-pinene (presenting also other monoterpenes: $\beta$-pinene, carene and limonene), cis-3-hexenol/hexanal as well as other VOCs not measured in this study. The ~~concentrations~~ mixing ratios 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 gradual increases (Fig. 4) and step-wise ~~changes and gradual increases of VOC concentrations (see Fig. ??)~~ changes (Fig. 5) of VOC mixing ratios, with 2-3 repetitions per instrument and test type. We tested six VOCs: $\beta$-pinene, ~~$\delta$~~$\Delta$3-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$_4$~~$CH_4$ and $N_2O$ were included in the spectra library ~~.~~ (i.e., interfering VOCs were

not included in the spectral library). We acknowledge that this is not a correct application of the analyser in the presence of known interference according to the manufacturers guidelines. We did so to evaluate the impact of VOCs missing in the spectral library due to unexpectedly occurring VOCs, unidentified compounds, or user errors on $CH_4$ flux measurements.

During experiment 2 and for the field measurements, we separately quantified the effect of adding a ~~missing VOC to~~ VOC present or missing in the spectral library. To do so, we analyzed the data twice, once with ~~minimal~~ limited 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~~ a full library that contained spectra of all tested VOCs (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.~~ mixing ratio and apparent $CH_4$ mixing ratio. To avoid effects of transient interferences, we excluded time points where VOC ~~concentrations~~ mixing ratios abruptly changed (>35% change in VOC ~~concentration~~ mixing ratio per minute). Repeated challenges with the same test were combined in one regression analysis, but ~~stepwise~~ step-wise 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 ~~$CH_4$~~ $CH_4$ concentrations in the in-house ~~pressurized~~ pressurised air supply, which limited our ability to detect small interferences. We used a bootstrap approach to calculate this uncertainty. For this, the measured ~~$CH_4$~~ $CH_4$ concentrations were replaced ~~those by~~ by those from 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 ~~$CH_4$~~ $CH_4$ concentrations represented true changes in ~~$CH_4$~~ $CH_4$ 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~~ Significant 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~~ calculated 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). All stated uncertainties refer to 95% confidence intervals.

## 2.5 Impact assessment for soil, stem, and shoot chambers

We assessed of the potential impact of VOC interferences on $CH_4$ flux measurements in three scenarios representing soil, stem, and shoot chamber measurements. The assumptions used for these estimates are shown in Table 1. Chamber dimensions and $CH_4$ and VOC flux rate, were chosen based on measurements conducted at SMEAR II LTER field station (Hyytiälä, Finland) (Hari and Kulmala, 2005).

Only monoterpens (PTR/MS signal at m/z 137) were taken into account, and it was assumed that these VOCs uniformly interfered with $CH_4$ measurements at the same rate as $\beta$-pinene. We furthermore assumed that VOC emission rates remain

constant over the chamber closure time, i.e., that chamber headspace VOC mixing ratios do not approach saturation during the closure. While this assumption is unlikely to hold true for shoot chambers, it allows us to conduct a worst case estimate for VOC interferences. For each chamber type, we assessed the effects of VOC emissions at typical (i.e., average) as well as peak (maximum) emission rates. For FTIR, were estimated the effects of both VOCs present in the spectral library (interference

5  measured on DX4040 with full library) and VOCs missing in the spectral library (interference on DX4040 with limited library).

Based on these assumptions, we calculated the actual change in $CH_4$ mixing ratios during a chamber closure, the VOC mixing ratio reached at the end of the chamber closure, the upper limit to the apparent $CH_4$ mixing ratio measured due to VOC interference on each analyser, and the maximum ratio of apparent to actual $CH_4$ emissions. We emphasise that this is only a

10  preliminary assessment of the impact of VOC interferences on $CH_4$ flux measurements, as neither the identity of all emitted VOCs nor their interference on different analysers are fully known. These results of these calculations should therefore be understood as order-of-magnitude estimates.

## 3  Results

### 3.1  Initial analysis of field data

15  Our initial ~~field~~ spruce stem measurements showed a stark discrepancy between stem ~~$CH_4$~~ $CH_4$ emissions measured with the LGR UGGA and the GASMET DX4040 analysers. Measurements conducted with the LGR UGGA ranged from an apparent ~~$CH_4$~~ $CH_4$ uptake of -2 $\mu$g ~~$CH_4$ $h^{-1}$ $m^{-2}$~~ $CH_4$ $h^{-1}$ $m^{-2}$ and an apparent ~~$CH_4$~~ $CH_4$ emission of 7 $\mu$g ~~$h^{-1}$ $m^{-2}$~~ $CH_4$ $h^{-1}$ $m^{-2}$ (Fig 1). Measurements conducted with the DX4040 (limited spectral library) consistently showed an apparent ~~$CH_4$~~ $CH_4$ uptake ranging with a much larger flux (-145 to +8 $\mu$g ~~$CH_4$ $h^{-1}$ $m^{-2}$) (Fig 1~~ $CH_4$ $h^{-1}$ $m^{-2}$). The average ~~$CH_4$~~ $CH_4$ fluxes were

20  +0.44 $\pm$ 0.15 $\mu$g ~~$CH_4$ $h^{-1}$ $m^{-2}$~~ $CH_4$ $h^{-1}$ $m^{-2}$ (LGR UGGA) and -17.4 $\pm$ 3.7 $\mu$g ~~$CH_4$ $h^{-1}$ $m^{-2}$~~ $CH_4$ $h^{-1}$ $m^{-2}$ (GASMET DX4040). In contrast, both analysers measured similar soil $CH_4$ fluxes, with average fluxes of -36.0 $\pm$ 7.9 (LGR UGGA) and -19.4 $\pm$ 5.3 $\mu$g $CH_4$ $h^{-1}$ $m^{-2}$ (GASMET DX4040).

### 3.2  Qualitative screening for interferences

An example for the changes in VOC ~~concentrations~~ mixing ratios over time produced by our setup is shown in Fig. 3a. The

25  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 $\beta$-pinene was inserted into the VOC source. This resulted in periodic patterns of presence and absence of $\beta$-pinene in the analysed air stream, with a maximum ~~concentration~~ mixing ratio of approximately 5 ~~ppm~~ ppmv.

The response of the ~~$CH_4$ analyzers~~ $CH_4$ analysers to the changing $\beta$-pinene ~~concentrations~~ mixing ratios is depicted in Fig.

30  3b-h. The FTIR-based analyser (DX4040) showed the strongest interference, with ~~$CH_4$~~ $CH_4$ readings reaching by up to ~~4ppm~~ 4 ppmv when $\beta$-pinene was added to the air stream, i.e., ~~2ppm~~ 2 ppmv above the actually ~~$CH_4$ concentration~~ $CH_4$ mixing ratio

(Fig. 3b). In contrast, measured CH$_4$ mixing ratios remained stable around 2ppmv 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 moderate interferences by *changes* in VOC mixing ratios (Fig. 3c). The sudden increase in the $\beta$-pinene mixing ratios resulted in temporary positive deviations corresponding to 20 ppbv CH$_4$ ppmv$^{-1}$ $\beta$-pinene. We also detected a negative deviation when VOCs were suddenly removed from the air stream. A similar, but much weaker ($\sim$1ppbv) 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 $\beta$-pinene to the air stream (Fig. 3e-f), however, for the G4301 analyser this was because relatively high noise and occasional outliers in the measured CH$_4$ mixing ratio may have masked potential small interferences. Finally, we did not detect any interference of $\beta$-pinene with the measured $\delta^{13}C_{CH4}$ values (Fig. 3g).

An overview of the interference tests with other VOCs is provided in Table 2. 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 $CH_4$ mixing ratio measurements on the Picarro G2301 and G2201i instruments were transient, similar to those shown for $\beta$-pinene (Fig. 3c).

Only two VOCs interfered with $\delta^{13}C_{CH4}$ measurements by the Picarro G2201. First, toluene, which was added at high mixing ratios (30 000 - 35 000 ppmv) lead to an apparent increase in $\delta^{13}C_{CH4}$ values by 1‰. Second, an accidental addition of high mixing ratios of methanol (>80 000 ppbv, 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 step-wise changes in VOC mixing ratios. As an example, the effects of gradual and step-wise changes in $\beta$-pinene mixing ratios on the apparent CH$_4$ mixing ratios measured by three different analysers are shown in Fig. 4a and Fig. 5a, respectively. In this experiment, we did not detect a significant effect of $\beta$-pinene mixing ratios on $CH_4$ mixing ratios measured with the Picarro G2301 (Figs. 4b,5b) or the LGR UGGA instruments (Figs. 4e,5e). In contrast, $\beta$-pinene led to a significant underestimation of $CH_4$ mixing ratios with the Gasmet DX4040 (by approximately 120 ppbv $CH_4$ ppmv$^{-1}$ $\beta$-pinene) when $\beta$-pinene was not part of the spectral library (Figs. 4c,5c). Including $\beta$-pinene (and other VOCs) in the spectra library significantly reduced this interference to approximately 1 ppbv $CH_4$ ppmv$^{-1}$ $\beta$-pinene (Figs. 4d,5d).

Similar results were found in tests with other VOCs. A list of the interferences quantified in different experiments is provided in Table 3. We did not detect a significant effect of VOC mixing ratios on the apparent CH$_4$ mixing ratios measured by the Picarro G2301 and the LGR UGGA. For $\beta$-pinene and $\Delta$3-carene we constrained the upper

confidence limits were <1 ~~ppb CH₄ ppm~~ ppbv CH$_4$ ppmv$^{-1}$ VOC on both instruments, for other compounds confidence limits were higher, mainly due to lower ~~concentrations~~ mixing ratios during the tests.

Interference on the Gasmet DX4040 without specific libraries for the tested compounds were high, ranging from -35 ~~ppb ppm~~ ppbv ppmv$^{-1}$ (methanol) to 1800 ~~ppb~~ ppbv ppm$^{-1}$ (cis-3-hexen-1-ol). Adding reference spectra of the tested VOCs to the

5  library substantially decreased the interferences, but significant interferences ~~weres~~ were still detected for $\beta$-pinene, 3-carene and hexenylacetate. (Table 3).

FTIR- and PTR-MS based measurements of VOC ~~concentrations~~ mixing ratios were highly correlated (R=0.956 to 0.998) for most compounds (Fig. 6). Poor correlations were found for linalool, which was present at ~~concentrations~~ mixing ratios close to or below the detection limit of the FTIR method (10 ~~ppb).~~ ppbv).

10  ### 3.4 Revised analysis of field data

After re-analysis with the full library, our field measurements by FTIR showed smaller ~~CH₄~~ CH$_4$ fluxes than in our initial analysis (Fig. 1). The methane emission rates generated in this revised analysis (-85 to +8 $\mu$g ~~CH₄ h⁻¹ m⁻²~~ CH$_4$ h$^{-1}$ m$^{-2}$), however, still showed a ~~substancial~~ substantial net uptake of ~~CH₄~~ CH$_4$. The average apparent ~~CH₄~~ CH$_4$ flux was -10.1 $\pm$ 1.6 $\mu$g ~~CH₄ h⁻¹ m⁻²~~ CH$_4$ h$^{-1}$ m$^{-2}$. Assuming that measurements conducted by OA-ICOS revealed the true ~~CH₄~~ CH$_4$ flux, the

15  re-analysis decreased the bias in FTIR based measurements by 41%. In contrast, the re-analysed of soil CH$_4$ fluxes resulted in slightly lower average flux (-19.1 $\pm$ 6.1 $\mu$g CH$_4$ h$^{-1}$ m$^{-2}$) compared to initial measurements with the limited library (-19.4 $\pm$ 5.3 $\mu$g CH$_4$ h$^{-1}$ m$^{-2}$).

### 3.5 Estimated impact on static chamber systems on different ecosystem compartments.

VOC (monoterpene) to methane emission ratios increased from soil to stem to shoot chambers, spanning over four orders if

20  magnitude (Table 1). The practical impact of VOC interferences on CH$_4$ strongly differed between ecosystem compartments. True CH$_4$ fluxes typically exceeded apparent CH$_4$ fluxes due to VOC interferences by 2 or more orders of magnitude in soil chambers, whereas the the upper limit of apparent CH$_4$ fluxes was equal or greater than true fluxes in shoot chambers (Fig. 7, Table 4).

Our impact estimates suggest the all analysers were able to accurately (<5% measurement error) quantify soil CH$_4$ fluxes at

25  average VOC emission rates, even if important VOCs are missing in the FTIR spectral library (Fig. 7. Stem flux measurements, in contrast, are more vulnerable to VOC interferences, with upper limits of confidence on the order of 2-6% of the actual CH$_4$ flux, except for FTIR with incomplete spectral libraries where apparent CH$_4$ fluxes were estimated to exceed to interference may exceed actual fluxes several fold.

VOC interferences are a serious challenge for quantifying CH$_4$ flux in shoot chambers where VOC fluxes are approximately

30  4 orders of magnitude higher than CH$_4$ fluxes. Our results show that apparent fluxes due to VOC interferences can exceed actual fluxes when shoot CH$_4$ fluxes are measured by FTIR, even if all VOCs are included in the spectral library. While we were not able to detect significant VOC interferences on OA-ICOS and CRDS based analysers, the upper limit of uncertainty of these interferences still allows for interferences that exceed actual CH$_4$ fluxes in shoot chambers.

## 4 Discussion

### 4.1 FTIR-based analysers

Our results show that ~~FTIR-based gas analysers are vulnerable to interferences from co-emitted VOCs .~~ FTIR based analysers are not well suited for measuring plant $CH_4$ fluxes and other applications that quantify small changes in $CH_4$ mixing ratios in the presence of much larger changes in the mixing ratios of other compounds, as is the case for plant $CH_4$ flux measurements (Tab. 4, Fig. 7). In particular, our work emphasises that FTIR based $CH_4$ flux measurements can only provide reliable data if all VOCs that co-emitted in relevant amounts are identified and included in the spectral library.

Measurements of plant ~~$CH_4$ emissions with enclosure chambers by this principle~~ $CH_4$ emissions with incomplete spectral libraries can result in gross over- or under-estimations of the actual ~~$CH_4$~~ $CH_4$ 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. The presence of VOCs missing in the spectral library is typically indicated by high residual values for the spectral fitting, such measurements should be re-analysed with an amended spectral library or, if this is not possible, considered invalid. Spectral libraries compiled for soil flux measurements are not sufficient for quantifying $CH_4$ fluxes from tree stems. Had we solely relied on ~~FTIR to quantify $CH_4$~~ an FTIR system with an incomplete spectral library intended from soil flux measurements to quantify $CH_4$ fluxes during our field campaign in Skogaryd, we would have identified spruce stems as a strong sink of ~~$CH_4$~~ $CH_4$ (Fig. 1). However, concurrent measurements by the OA-ICOS-based LGR UGGA, which were largely unaffected by VOC co-emissions (Table 3), revealed that these trees stems actually act as a small source of ~~$CH_4$~~$CH_4$. 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 ~~$CH_4$~~$CH_4$ measurements, including methanol, $\beta$-pinene, and hexenylacetate. The effect of these VOCs outweighted the positive interference of other VOCs including $\Delta$3-carene and hexenol. It is, however, important to note that we did not quantify the intefereces of all potential VOCs, including the dominant compound emitted by spruce trees ($\alpha$-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 3. 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 ($\beta$-pinene, $\Delta$3-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~~ In contrast, FTIR and OA-ICOS based analysers measured similar $CH_4$ fluxes from soil chambers. This shows that both measurement principles can reliably quantify soil $CH_4$ fluxes, where the VOC:methane flux ratio is significantly lower than in tree stems and shoots, which is consistent with previous studies (e.g. Falk et al., 2014). Our study furthermore showed that FTIR-based 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~~ mixing ratios quantified by FTIR and PTR-MS (Fig 6) indicates that FTIR can conduct precise measurements of VOC ~~concentrations.~~ mixing ratios. 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

5 VOC ~~concentrations~~ mixing ratios (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.~~ mixing ratios.

### 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

10 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~~ the VOC mixing ratio resulted in minor deviations of the measured ~~CH₄ concentration.~~ $CH_4$ mixing ratios. 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~~ mixing ratios of VOCs and ~~CH₄~~ $CH_4$ increase gradually (e.g., over a 20–40 minutes chamber closure).

15 These interferences may, however, pose an important bias for measurements that rely on fast measurements of air masses with changing VOC ~~concentrations,~~ mixing ratios as used for ~~Eddy~~ eddy covariance (EC) measurements. In these measurements, interferences from VOC emissions as detected in this study could potentially lead to an overestimation of ~~CH₄~~ $CH_4$ emissions. We have, however, not been able to further investigate VOC interferences on the high-frequency analysers used for EC measurements.

20 ## 5 Conclusions

We quantified the interference of VOCs on ~~CH₄~~ $CH_4$ 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~~

25 ~~CH₄ fluxes~~ FTIR based analysers are therefore not well suited for studies of plant $CH_4$ fluxes and other applications where small $CH_4$ fluxes need to be quantified in the presence of much higher fluxes of VOCs. Our results, however, ~~indicate that using the correct spectrum libraries,~~ also indicate that FTIR instruments can be a cost-effective solution to field measurements of certain VOCs.

# References

Aaltonen, H., Aalto, J., Kolari, P., Pihlatie, M., Pumpanen, J., Kulmala, M., Nikinmaa, E., Vesala, T., and Bäck, J.: Continuous VOC flux measurements on boreal forest floor, Plant and Soil, 369, 241–256, https://doi.org/10.1007/s11104-012-1553-4, http://link.springer.com/10.1007/s11104-012-1553-4, 2013.

5  Assan, S., Baudic, A., Guemri, A., Ciais, P., Gros, V., and Vogel, F. R.: Characterization of interferences to in situ observations of $\delta$13CH4 and C2H6 when using a cavity ring-down spectrometer at industrial sites, Atmospheric Measurement Techniques, 10, 2077–2091, https://doi.org/10.5194/amt-10-2077-2017, https://www.atmos-meas-tech.net/10/2077/2017/, 2017.

Carmichael, M. J., Bernhardt, E. S., Bräuer, S. L., and Smith, W. K.: The role of vegetation in methane flux to the atmosphere: Should vegetation be included as a distinct category in the global methane budget?, Biogeochemistry, 119, 1–24, https://doi.org/10.1007/s10533-014-9974-1, 2014.

10  Covey, K. R. and Megonigal, J. P.: Methane production and emissions in trees and forests, https://doi.org/10.1111/nph.15624, 2019.

Etiope, G.: Detecting and Measuring Gas Seepage, in: Natural Gas Seepage, pp. 63–84, Springer International Publishing, Cham, https://doi.org/10.1007/978-3-319-14601-0_4, http://link.springer.com/10.1007/978-3-319-14601-0_4, 2015.

Falk, J. M., Schmidt, N. M., and Ström, L.: Effects of simulated increased grazing on carbon allocation patterns in a high arctic mire, Biogeochemistry, 119, 229–244, https://doi.org/10.1007/s10533-014-9962-5, http://link.springer.com/10.1007/s10533-014-9962-5, 2014.

Franz, D., Acosta, M., Altimir, N., Arriga, N., Arrouays, D., Aubinet, M., Aurela, M., Ayres, E., López-Ballesteros, A., Barbaste, M., Berveiller, D., Biraud, S., Boukir, H., Brown, T., Brümmer, C., Buchmann, N., Burba, G., Carrara, A., Cescatti, A., Ceschia, E., Clement, R., Cremonese, E., Crill, P., Darenova, E., Dengel, S., D'Odorico, P., Gianluca, F., Fleck, S., Fratini, G., Fuß, R., Gielen, B., Gogo, S., Grace, J., Graf, A., Grelle, A., Gross, P., Grünwald, T., Haapanala, S., Hehn, M., Heinesch, B., Heiskanen, J., Herbst, M., Herschlein, C., Hörtnagl, L., Hufkens, K., Ibrom, A., Jolivet, C., Joly, L., Jones, M., Kiese, R., Klemedtsson, L., Kljun, N., Klumpp, K., Kolari, P., Kolle, O., Kowalski, A., Kutsch, W., Laurila, T., Ligne, A. D., Linder, S., Lindroth, A., Lohila, A., Longdoz, B., Mammarella, I., Manise, T., Marañon-Jimenez, S., Matteucci, G., Mauder, M., Meier, P., Merbold, L., Mereu, S., Metzger, S., Migliavacca, M., Mölder, M., Montagnani, L., Moureaux, C., Nelson, D., Nemitz, E., Nicolini, G., Nilsson, M., Beeck, M. O. d., Osborne, B., Löfvenius, M. O., Pavelka, M., Peichl, M., Peltola, O., Pihlatie, M., Pitacco, A., Pokorny, R., Pumpanen, J., Ratié, C., Schrumpf, M., Sedlák, P., Ortiz, P. S., Siebicke, L., Šigut, L., Silvennoinen, H., Simioni, G., Skiba, U., Sonnentag, O., Soudani, K., Soulé, P., Steinbrecher, R., Tallec, T., Thimonier, A., Tuittila, E., Tuovinen, J., Vestin, P., Vincent, G., Vincke, C., Vitale, D., Waldner, P., Weslien, P., Wingate, L., Wohlfahrt, G., Zahniser, M., and Vesala, T.: Towards long-term standardised carbon and greenhouse gas observations for monitoring Europe's terrestrial ecosystems: a review, International Agrophysics, 32, 439–455, https://doi.org/10.1515/intag-2017-0039, 2018.

Grabmer, W., Kreuzwieser, J., Wisthaler, A., Cojocariu, C., Graus, M., Rennenberg, H., Steigner, D., Steinbrecher, R., and Hansel, A.: VOC emissions from Norway spruce (Picea abies L. [Karst]) twigs in the field—Results of a dynamic enclosure study, Atmospheric Environment, 40, 128–137, https://doi.org/10.1016/J.ATMOSENV.2006.03.043, https://www.sciencedirect.com/science/article/pii/S135223100600327X, 2006.

Hari, P. and Kulmala, M.: Station for Measuring Ecosystem–Atmosphere Relations (SMEAR II), Boreal Env. Res., 10, 315–322, 2005.

Janson, R. W.: Monoterpene emissions from Scots pine and Norwegian spruce, Journal of Geophysical Research: Atmospheres, 98, 2839–2850, https://doi.org/10.1029/92JD02394, http://doi.wiley.com/10.1029/92JD02394, 1993.

35  Jurasinski, G., Huth, V., Hofmann, M., Schmidt, M., and Hofmann, J.: Comparing laser-based gas analyzers for greenhouse gas measurements with closed chambers – precision and field applicability, in: European Geosciences Union General Assembly, vol. 21, p. 11049, 2019.

Kandel, T. P., Gowda, P. H., Somenahally, A., Northup, B. K., DuPont, J., and Rocateli, A. C.: Nitrous oxide emissions as influenced by legume cover crops and nitrogen fertilization, Nutrient Cycling in Agroecosystems, 112, 119–131, https://doi.org/10.1007/s10705-018-9936-4, http://link.springer.com/10.1007/s10705-018-9936-4, 2018.

Keppler, F., Hamilton, J. T. G., Braß, M., and Röckmann, T.: Methane emissions from terrestrial plants under aerobic conditions, Nature, 439, 187–191, https://doi.org/10.1038/nature04420, 2006.

Klemedtsson, L., Ernfors, M., Björk, R. G., Weslien, P., Rütting, T., Crill, P., and Sikström, U.: Reduction of greenhouse gas emissions by wood ash application to a Picea abies (L.) Karst. forest on a drained organic soil, European Journal of Soil Science, 61, 734–744, https://doi.org/10.1111/j.1365-2389.2010.01279.x, http://doi.wiley.com/10.1111/j.1365-2389.2010.01279.x, 2010.

Machacova, K., Bäck, J., Vanhatalo, A., Halmeenmäki, E., Kolari, P., Mammarella, I., Pumpanen, J., Acosta, M., Urban, O., and Pihlatie, M.: Pinus sylvestris as a missing source of nitrous oxide and methane in boreal forest, Scientific Reports, 6, 1–8, https://doi.org/10.1038/srep23410, http://dx.doi.org/10.1038/srep23410, 2016.

Nisbet, R. E., Fisher, R., Nimmo, R. H., Bendall, D. S., Crill, P. M., Gallego-Sala, A. V., Hornibrook, E. R., López-Juez, E., Lowry, D., Nisbet, P. B., Shuckburgh, E. F., Sriskantharajah, S., Howe, C. J., and Nisbet, E. G.: Emission of methane from plants, Proceedings of the Royal Society B: Biological Sciences, 276, 1347–1354, https://doi.org/10.1098/rspb.2008.1731, http://www.royalsocietypublishing.org/doi/10.1098/rspb.2008.1731, 2009.

Pangala, S. R., Hornibrook, E. R., Gowing, D. J., and Gauci, V.: The contribution of trees to ecosystem methane emissions in a temperate forested wetland, Global Change Biology, 21, 2642–2654, https://doi.org/10.1111/gcb.12891, http://doi.wiley.com/10.1111/gcb.12891, 2015.

Pangala, S. R., Enrich-Prast, A., Basso, L. S., Peixoto, R. B., Bastviken, D., Hornibrook, E. R., Gatti, L. V., Marotta, H., Calazans, L. S. B., Sakuragui, C. M., Bastos, W. R., Malm, O., Gloor, E., Miller, J. B., and Gauci, V.: Large emissions from floodplain trees close the Amazon methane budget, Nature, 552, 230–234, https://doi.org/10.1038/nature24639, http://dx.doi.org/10.1038/nature24639, 2017.

Pitz, S. and Megonigal, J. P.: Temperate forest methane sink diminished by tree emissions, New Phytologist, 214, 1432–1439, https://doi.org/10.1111/nph.14559, http://doi.wiley.com/10.1111/nph.14559, 2017.

Pitz, S. L., Megonigal, J. P., Chang, C. H., and Szlavecz, K.: Methane fluxes from tree stems and soils along a habitat gradient, Biogeochemistry, 137, 307–320, https://doi.org/10.1007/s10533-017-0400-3, https://doi.org/10.1007/s10533-017-0400-3, 2018.

R Development Core Team: R: A Language and Environment for Statistical Computing, http://www.r-project.org, 2015.

Rapson, T. D. and Dacres, H.: Analytical techniques for measuring nitrous oxide, TrAC Trends in Analytical Chemistry, 54, 65–74, https://doi.org/10.1016/J.TRAC.2013.11.004, https://www.sciencedirect.com/science/article/pii/S0165993613002574, 2014.

Rella, C. W., Hoffnagle, J., He, Y., and Tajima, S.: Local- and regional-scale measurements of CH4, Δ13CH4, and C2H6 in the Uintah Basin using a mobile stable isotope analyzer, Atmospheric Measurement Techniques, 8, 4539–4559, https://doi.org/10.5194/amt-8-4539-2015, 2015.

Rinne, H., Guenther, A., Greenberg, J., and Harley, P.: Isoprene and monoterpene fluxes measured above Amazonian rainforest and their dependence on light and temperature, Atmospheric Environment, 36, 2421–2426, https://doi.org/10.1016/S1352-2310(01)00523-4, https://www.sciencedirect.com/science/article/pii/S1352231001005234, 2002.

Rissanen, K., Hölttä, T., Vanhatalo, A., Aalto, J., Nikinmaa, E., Rita, H., and Bäck, J.: Diurnal patterns in Scots pine stem oleoresin pressure in a boreal forest, Plant, Cell & Environment, 39, 527–538, https://doi.org/10.1111/pce.12637, http://doi.wiley.com/10.1111/pce.12637, 2016.

Simpson, D., Winiwarter, W., Börjesson, G., Cinderby, S., Ferreiro, A., Guenther, A., Hewitt, C. N., Janson, R., Khalil, M. A. K., Owen, S., Pierce, T. E., Puxbaum, H., Shearer, M., Skiba, U., Steinbrecher, R., Tarrasón, L., and Öquist, M. G.: Inventorying emissions from nature in Europe, Journal of Geophysical Research: Atmospheres, 104, 8113–8152, https://doi.org/10.1029/98JD02747, http://doi.wiley.com/10.1029/98JD02747, 1999.

5  Taipale, R., Ruuskanen, T. M., Rinne, J., Kajos, M. K., Hakola, H., Pohja, T., and Kulmala, M.: Technical Note: Quantitative long-term measurements of VOC concentrations by PTR-MS &amp;ndash; measurement, calibration, and volume mixing ratio calculation methods, Atmospheric Chemistry and Physics, 8, 6681–6698, https://doi.org/10.5194/acp-8-6681-2008, http://www.atmos-chem-phys.net/8/6681/2008/, 2008.

Tarvainen, V., Hakola, H., Hellén, H., Bäck, J., Hari, P., and Kulmala, M.: Temperature and light dependence of the VOC emissions of Scots
10  pine, Atmospheric Chemistry and Physics, 5, 989–998, https://doi.org/10.5194/acp-5-989-2005, http://www.atmos-chem-phys.net/5/989/2005/, 2005.

Teutscherova, N., Vazquez, E., Arango, J., Arevalo, A., Benito, M., and Pulleman, M.: Native arbuscular mycorrhizal fungi increase the abundance of ammonia-oxidizing bacteria, but suppress nitrous oxide emissions shortly after urea application, Geoderma, 338, 493–501, https://doi.org/10.1016/J.GEODERMA.2018.09.023, https://www.sciencedirect.com/science/article/pii/S001670611831084X, 2019.

15  Vanhatalo, A., Chan, T., Aalto, J., Korhonen, J. F., Kolari, P., Hölttä, T., Nikinmaa, E., and Bäck, J.: Tree water relations can trigger monoterpene emissions from Scots pine stems during spring recovery, Biogeosciences, 12, 5353–5363, https://doi.org/10.5194/bg-12-5353-2015, https://www.biogeosciences.net/12/5353/2015/, 2015.

Warlo, H., Machacova, K., Nordstrom, N., Maier, M., Laemmel, T., Roos, A., and Schack-Kirchner, H.: Comparison of portable devices for sub-ambient concentration measurements of methane (CH $_4$ ) and nitrous oxide (N $_2$ O) in soil research,
20  International Journal of Environmental Analytical Chemistry, 98, 1030–1037, https://doi.org/10.1080/03067319.2018.1517871, https://www.tandfonline.com/doi/full/10.1080/03067319.2018.1517871, 2018.

Warner, D. L., Villarreal, S., McWilliams, K., Inamdar, S., and Vargas, R.: Carbon Dioxide and Methane Fluxes From Tree Stems, Coarse Woody Debris, and Soils in an Upland Temperate Forest, Ecosystems, 20, 1205–1216, https://doi.org/10.1007/s10021-016-0106-8, http://link.springer.com/10.1007/s10021-016-0106-8, 2017.

25  Zellweger, C., Emmenegger, L., Firdaus, M., Hatakka, J., Heimann, M., Kozlova, E., Spain, T. G., Steinbacher, M., van der Schoot, M. V., and Buchmann, B.: Assessment of recent advances in measurement techniques for atmospheric carbon dioxide and methane observations, Atmospheric Measurement Techniques, 9, 4737–4757, https://doi.org/10.5194/amt-9-4737-2016, https://www.atmos-meas-tech.net/9/4737/2016/, 2016.

Zhao, Y., Pan, Y., Rutherford, J., and Mitloehner, F. M.: Estimation of the interference in Multi-Gas measurements using infrared photoa-
30  coustic analyzers, Atmosphere, 3, 246–265, https://doi.org/10.3390/atmos3020246, 2012.
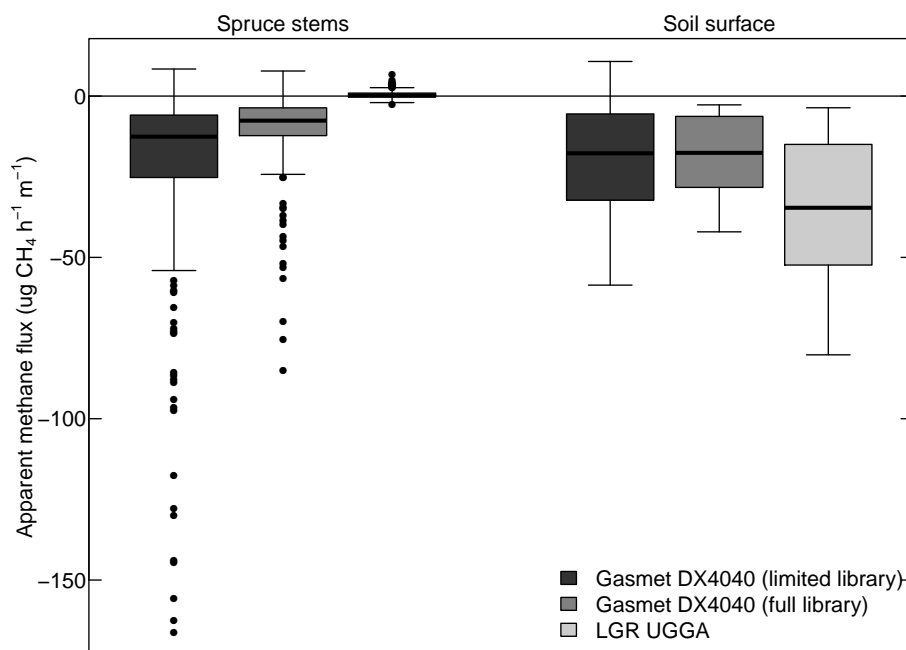
**Figure 1.** Apparent tree stem methane fluxes when quantified with a laser spectroscopy based analyser (LGR UGGA) and a FTIR based analyser (Gasmet DX4040). FTIR based fluxes are shown calculated based on spectral deconvolution with a minimal library that did not contain VOC spectra (min. lib.), and with a library that contained spectra of commonly occurring VOCs (full lib.).
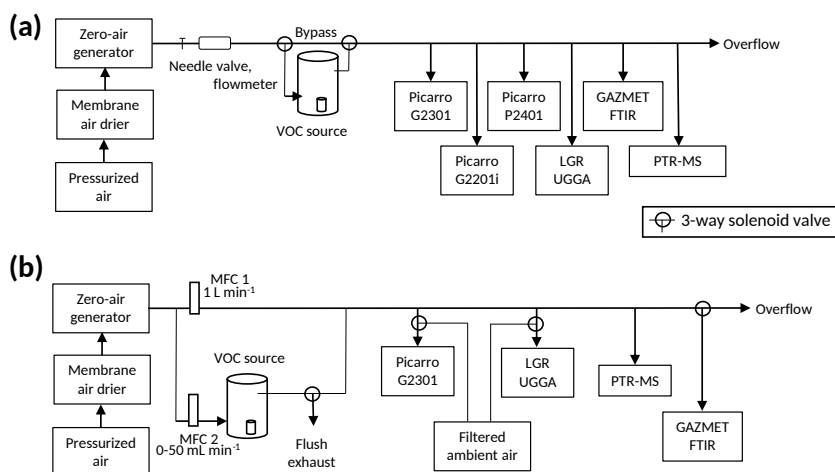


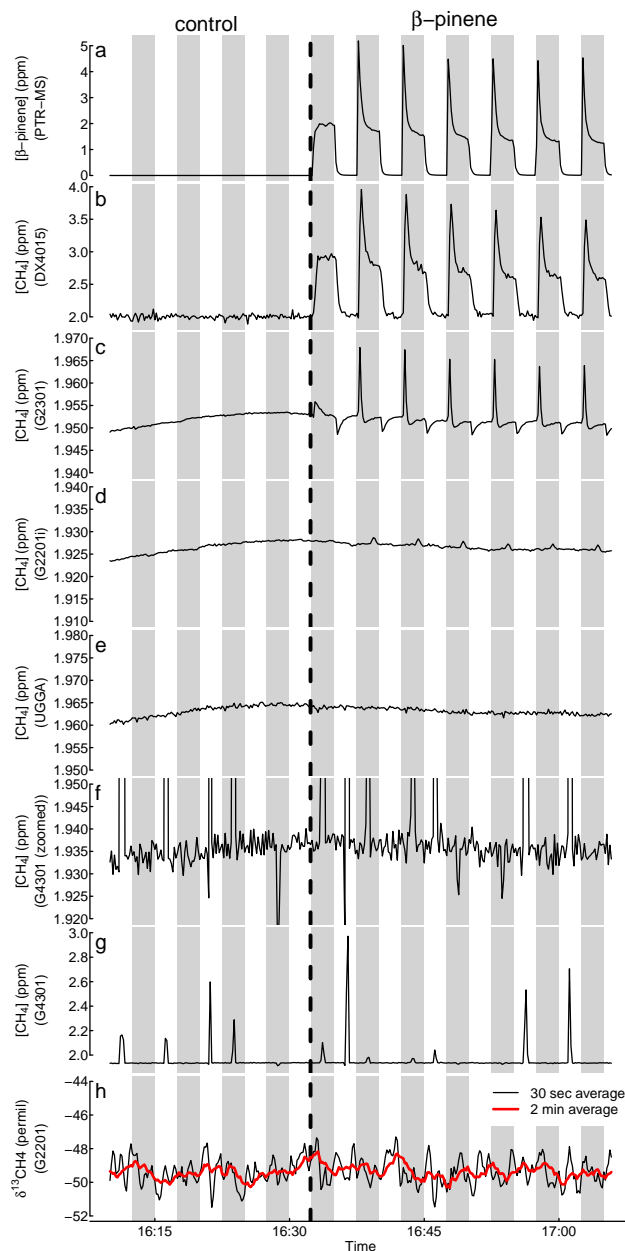**Figure 2.** Schematic for air flow in laboratory test 1 (panel **a**) and 2 (panel **b**).

**Figure 3.** ~~Development~~ Exemplary results from Experiment 1, shown for tests conducted with $\beta$-pinene. The panels show the development of ~~VOC~~ the $\beta$-pinene (panel **a**) ~~concentration~~ mixing ratio as measured by PTR-MS and apparent ~~CH₄ concentration~~ CH$_4$ mixing ratio as measured by Gasmet DX4015 (using an incomplete library intended for soil flux measurements), Picarro G2301, Picarro G2201i, LGR UGGA and Picarro G4301 (panels **b–g**, respectively) and $\delta^{13}$~~C-CH₄~~ 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, $\beta$-pinene vial was introduced into the standard source. Black line represents 10-second moving average of apparent ~~CH₄ concentrations~~ CH$_4$ mixing ratios 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**.
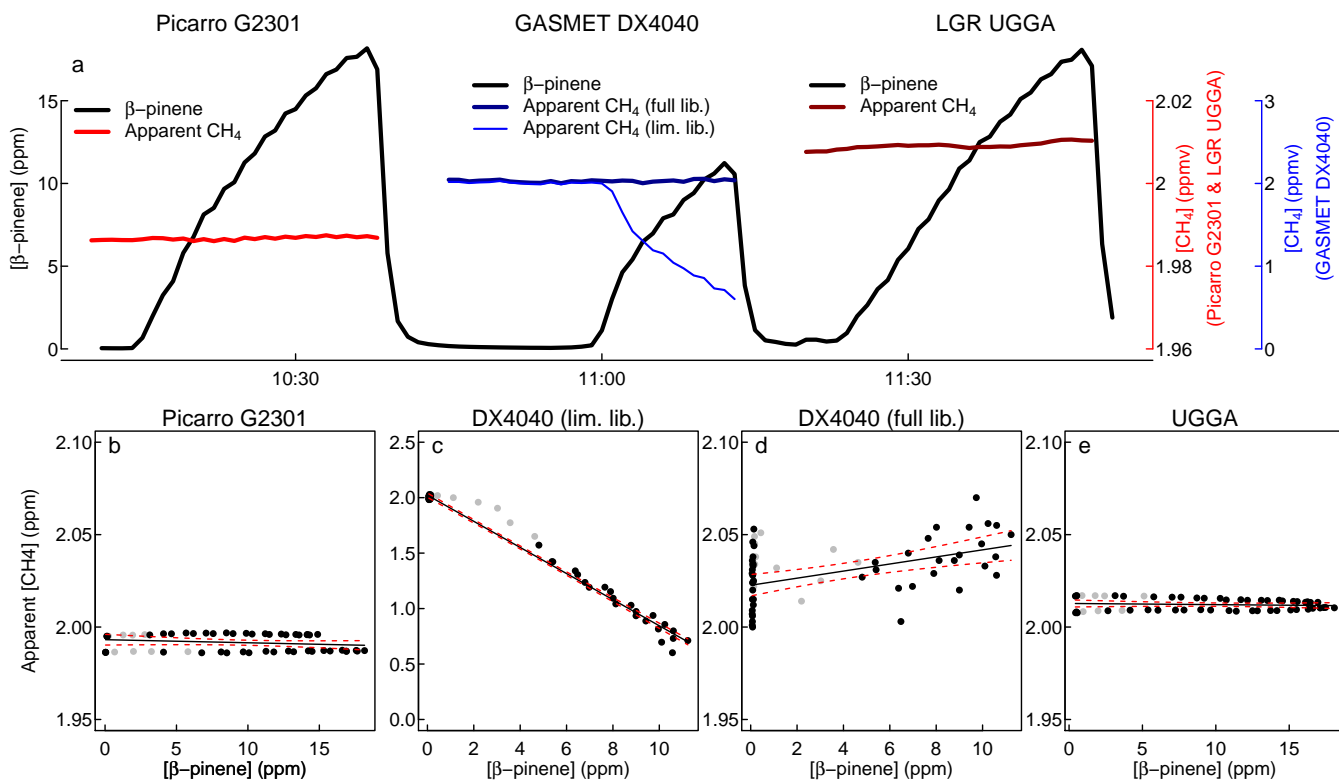
16

**Figure 4.** Quantitative measurements of the effect of $\beta$-pinene ~~concentrations~~ mixing ratios on ~~the~~ measured (apparent) methane ~~concentration~~ mixing ratios when analysers were challenged with a gradual increase ~~(a-f) or stepwise changes~~ in ~~the~~ $\beta$-pinene ~~concentrations (g-i)~~ mixing ratio . The figure depicts ~~both~~ an example for the time course of $\beta$-pinene and apparent ~~CH₄ concentrations~~ CH₄ mixing ratios (**a-b**; ~~g-h~~ a) ~~and~~ as well as the relationship between $\beta$-pinene and the measured ~~CH₄ concentration~~ CH₄ mixing ratio (**c-f; i-l** b-e). Note that in panel a, CH₄ concentrations measured by the Gasmet DX4040 analyser are depicted on a different scale (blue) than those measured by the Picarro G2301 and LGR UGGA analysers (red). Black lines in panels ~~c-f and i-l~~ b-e indicate linear regressions, dashed red lines the 95% confidence interval of these regressions. Data points that occurred after after a rapid changes in the $\beta$-pinene ~~concentration~~ mixing ratio and that were therefore excluded from the regression analysis are depicted in grey.
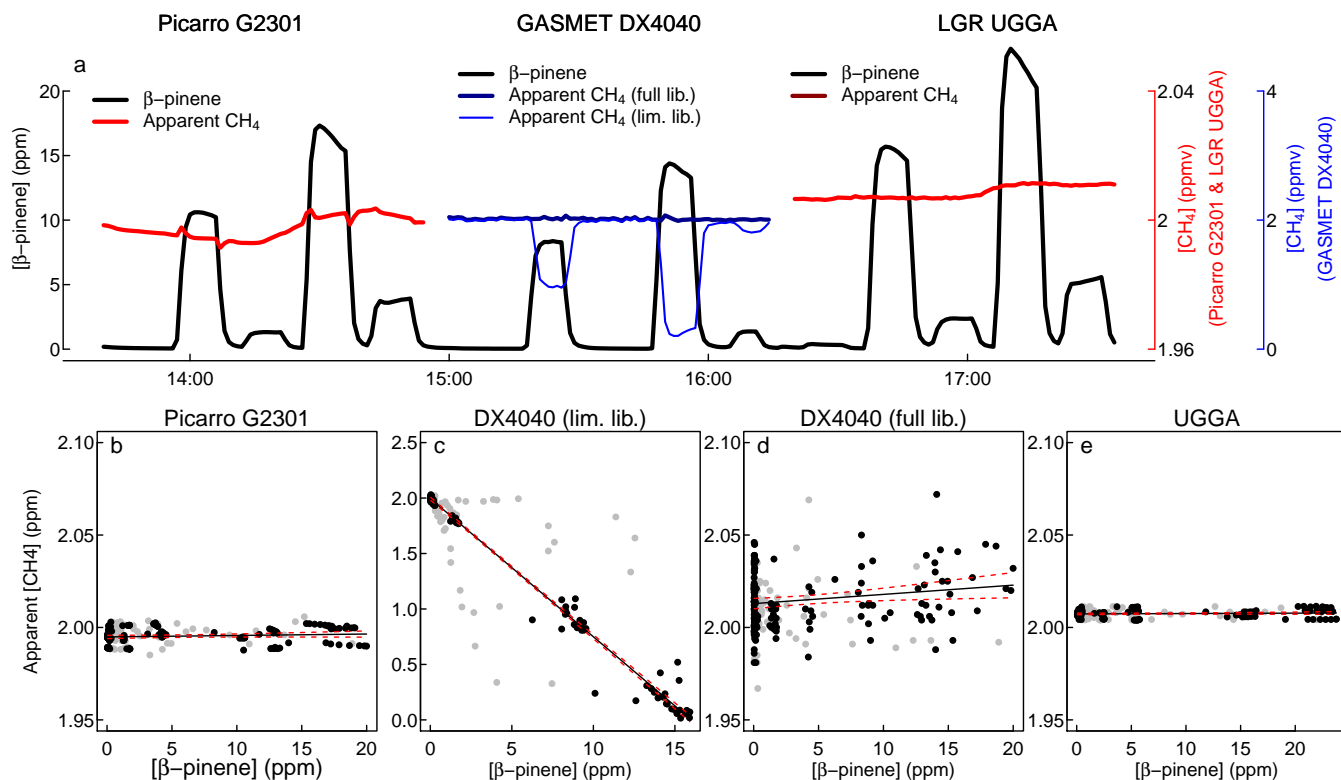
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**Figure 5.** Quantitative measurements of the effect of $\beta$-pinene mixing ratios on measured (apparent) methane mixing ratios when analysers were challenged with stepwise changes in the $\beta$-pinene mixing ratio . The figure depicts an example for the time course of $\beta$-pinene and apparent $CH_4$ mixing ratios (**a**) as well as the relationship between $\beta$-pinene and the measured $CH_4$ mixing ratio (**b-e**). Note that in panel a, $CH_4$ concentrations measured by the Gasmet DX4040 analyser are depicted on a different scale (blue) than those measured by the Picarro G2301 and LGR UGGA analysers (red). Black lines in panels b-e indicate linear regressions, dashed red lines the 95% confidence interval of these regressions. Data points that occurred after after a rapid changes in the $\beta$-pinene mixing ratio and that were therefore excluded from the regression analysis are depicted in grey.
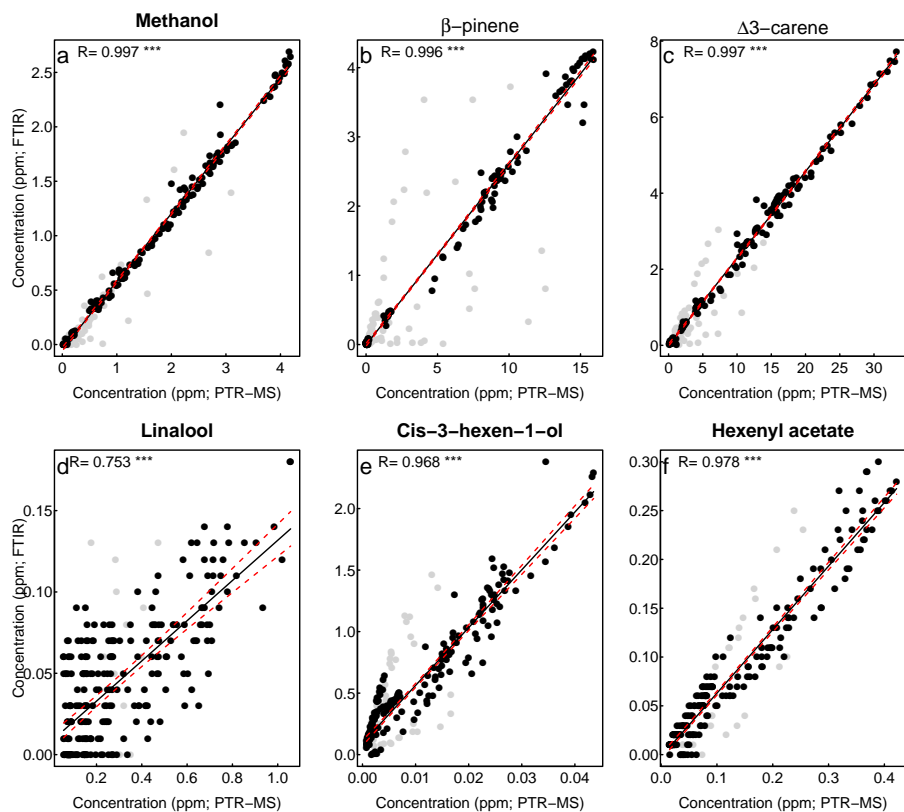
**Figure 6.** Correlation between FTIR- and PTR-MS based measurements of VOC ~~concentrations~~mixing ratios. Data points plotted in grey were excluded after rapid changes in the VOC ~~concentrations~~mixing ratio. Asterisks indicate ~~significante~~ significant levels: *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$.
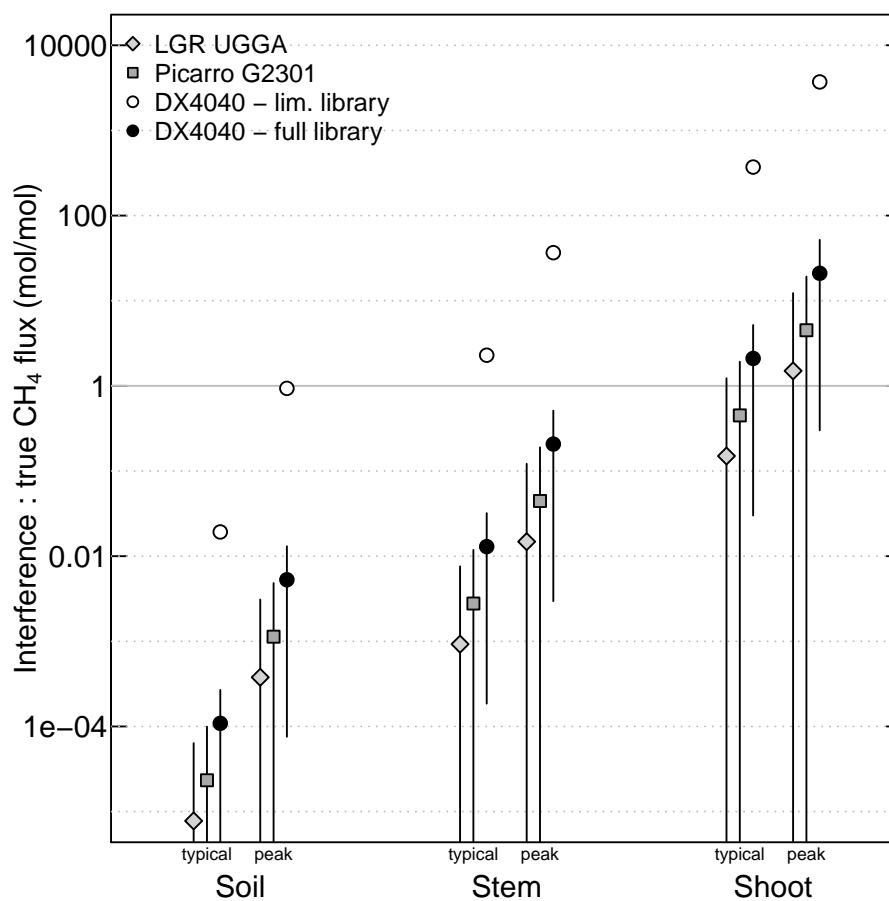
**Figure 7.** Estimated size of the $CH_4$ flux measurement error due to VOC interference (at typical and peak VOC fluxes) relative to the mean actual $CH_4$ fluxes in soil, stem, and shoot chambers. Assumptions underlying these estimates are shown in Table 1. Only monoterpens (m/z=137 in PTR-MS measurements) were taken into account for this estimate, and it was assumed that all monoterpens interfere with CH4 analysers the same rate as $\beta$-pinene. The results presented here should therefore be understood as order-of-magnitude estimates. Symbols indicate medians with error bars indicate the analytical uncertainty (95% confidence interval) associated with the quantification of VOC interferences (but do not take into account uncertainties in other assumptions).

**Table 1.** Assumptions used to estimate VOC effects on $CH_4$ flux measurements in static soil, stem, and shoot chambers. Where available, assumptions are based on measurements conducted in the Scots pine forest at the SMEAR II research station (Hyytiälä, Finland).

Sources: [1] Machacova et al. (2016) [2] Machacova et al. (2016) [3] Estimate based on Keppler et al. (2006)) [4] Aaltonen et al. (2013) [5] Vanhatalo et al. (2015); Rissanen et al. (2016) [6] Tarvainen et al. (2005)

**Table 2.** Summary of interferences detected in qualitative tests

| Compound | | Interference (ppbv apparent $CH_4$) | | | | |
|---|---|---|---|---|---|---|
| name | conc. range (~~ppb~~ppbv) [ion] | Gasmet DX4015 | Picarro G2301 | Picarro G2201i | Picarro G4301 | LGR UGGA |
| Methanol | 6 000 - 10 000 [33] | 500 - 700 | 15[a] | 2[a] | – | 2 |
| $\alpha$-pinene | 4 000 - 5 000 [137] | 1 500 – 2 000 | 10-15[a] | 1[a] | – | – |
| $\beta$-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 mixing ratio rather that presence of VOC

**Table 3.** Quantified interferences of volatile organic compounds on ~~CH₄~~ CH$_4$ analysers. Significant interferences are indicated indicated in bold.

| | | Interference (ppbv apparent CH$_4$ per ppmv VOC; 95% CI) | | | |
|---|---|---|---|---|---|
| | | Picarro G2301 | LGR UGGA | Gasmet DX 4040 ~~w/ lib~~ (full library) | Gasmet DX 4040 ~~w/o lib~~ (lim. library) |
| 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)** |
| $\beta$-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)** |
| $\Delta$3-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)** |

**Table 4.** Estimated impact of VOC interferences on methane flux measurements based on literature data of $CH_4$ and VOC fluxes.

| Chamber type | Soil chamber (upland) | | Stem chamber | | Shoot chamber | |
|---|---|---|---|---|---|---|
| VOC emission scenario | typical | peak | typical | peak | typical | peak |

[a] Monoterpene mixing ratios at the end of a chamber closure, estimated based on the flux rates, chamber characteristics, and closure times stated in Table 1. We assumed that fluxes remained constant throughout the chamber closure period. Monoterpene saturation in the chamber headspace may decrease monoterpene emission rates during chamber closure.

[b] Change in $CH_4$ mixing ratio during chamber closure, estimated based on assumptions stated in Table , estimated based on the flux rates, chamber characteristics, and closure times stated in Table 1.

[c] Upper confidence interval for the false $\Delta CH_4$ detected due to monoterpene interference with $CH_4$ mixing ratio measurements.

[d] Ratio of the error in $CH_4$ flux measrement due to monoterpene interference to the actual $CH_4$ flux.