Towards reliable measurements of trace gas fluxes at plant surfaces.

Kohl, Lukas

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Letters

Towards reliable measurements of trace gas fluxes at plant surfaces

Comment on Machacova *et al*. (2021) 'Trees as net sinks for methane (CH_4) and nitrous oxide (N_2O) in the lowland tropical rain forest on volcanic Réunion Island'

In their article, Katerina Machacova and coauthors (Machacova *et al.*, 2021) reported methane (CH_4) flux measurements between the atmosphere and tropical trees and/or their epiphytes. This research is timely and important, given the largely unknown role of trees in the CH_4 and N_2O cycles (Carmichael *et al.*, 2014; Barba *et al.*, 2019; Covey & Megonigal, 2019). Machacova and coauthors reported that tree stems and cryptogams constitute a novel sink of both CH_4 and N_2O based on these measurement data, a so-far unreported finding. In this Letter, we raise two major concerns about the study that – in our opinion – leaves this conclusion insufficiently supported by their data. First, we think it is likely that the method applied is unsuitable for this type of analysis and that the reported results may represent a measurement artefact rather than real trace gas fluxes. Second, we think that the authors provide insufficient information on the measurement method for readers to judge the validity of the analytical method. Based on the publication by Machacova and coauthors, we suggest principles that should be followed to ensure that published data on trace gas fluxes at plant surfaces are both reliable and reproducible.

Our main concerns stem from the use of a gas analyser in this study, which uses Fourier transform infrared (FTIR) spectroscopy for measuring trace gas concentrations. This FTIR method measures the broad infrared spectrum of an air sample and uses spectral deconvolution to quantify the concentrations of multiple gas species simultaneously. In our technical note (Kohl *et al.*, 2019), we demonstrate that this approach is particularly sensitive to interference from volatile organic compounds (VOCs). This interference is especially true for compounds missing in the spectral library used for deconvolution. We observed both positive (overestimation of CH_4 concentrations) and negative (underestimations of CH_4 concentrations) interferences, depending on the VOC present. These spectral interferences were between 0.036 and 2.2 ppbv apparent CH_4 per ppbv VOC present in the gas sample. Possible interferences of VOCs to the N_2O analysis of this analyser were not tested in our study.

These interferences pose a serious challenge for FTIR-based trace gas flux measurements at plant surfaces. VOCs including monoterpenes, isoprene, and methanol are emitted by plants at much higher rates than the trace gases (CH_4 and N_2O) typically measured from plant enclosures, such as in the paper by Machacova and coauthors. Specifically, we found that the presence of the commonly plant-emitted VOCs can cause the device to overestimate or underestimate CH_4 present in the sample gas. These VOCs occur in forest air at the low ppb range. However, as these compounds are constantly emitted by plant surfaces (e.g. Aalto *et al.*, 2014), they can accumulate to significant concentrations in static chambers used to estimate CH_4 and N_2O fluxes, therefore potentially significantly affecting the measurement signal with FTIR analysers.

We found that major VOC interferences (>100 ppbv apparent CH_4) can already occur at sub-ppm (>100 ppbv VOC) concentrations and that such interferences increase with increasing VOC concentration. This stresses the importance of accounting for the VOCs accumulating in closed static chambers, as such interferences would appear similar to actual CH_4 fluxes. This effect was particularly strong when the interfering VOCs were not included in the spectral library used for the deconvolution. To our knowledge, the Gasmet DX4015/DX4040 instruments have not been successfully validated against robust methods (e.g. gas chromatography, GC) for chamber flux measurements from plant surfaces.

What particularly raised our concern regarding the results of the paper by Machacova and coauthors is that they report tree stem CH_4 uptake rates being similar in magnitude to that measured by our group in a mature spruce forest in Sweden, using the same instrumentation (Kohl *et al.*, 2019). In Kohl *et al.* (2019), we quantified the CH_4 fluxes from mature spruce stems by both Gasmet DX4040 and LGR UGGA analysers. In contrast with the Gasmet device, the LGR UGGA uses a narrow spectrum infrared laser to measure trace gases based on their absorbance at very specific wavelengths (Baer *et al.*, 2002; Maddaloni *et al.*, 2006). We detected a strong apparent uptake of CH_4 when measured by the D4040 that could not be reproduced by the LGR UGGA (see Fig. 1). Subsequent laboratory experiments (Kohl *et al.*, 2019) revealed that these differences resulted from spectral interferences by VOCs on the Gasmet DX4040.

Unfortunately, Machacova and coauthors provide little information that would allow the reader to independently assess the validity of their measurement. Most essentially, the authors do not report which VOC species were included in the spectral library used for this study and do not provide any quality criteria applied to the spectral deconvolution (e.g. residual fits). Furthermore, the authors provide no information to determine if all major VOCs typically emitted from tree stems (Courtois *et al.*, 2012; Rissanen *et al.*, 2018; Vanhatalo *et al.*, 2020) were included in the library, or if flux measurements by the DX4015 were validated in any other form. Taken together, these omissions leave the reader unable to fully judge the validity of the reported results or to independently

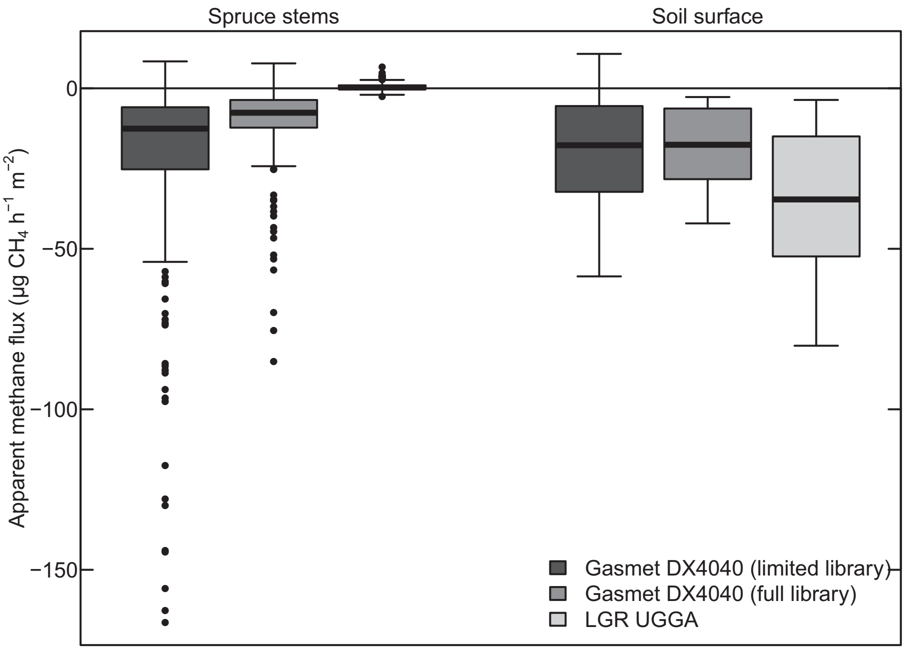

Fig. 1 Apparent CH_4 flux from soils and tree stems in a boreal forest stand, as measured using Fourier transform infrared (FTIR) spectroscopy (Gasmet DX4040) and laser absorption spectroscopy (LGR UGGA). Spectral deconvolution for FTIR was conducted with a full or limited spectral libraries. Figure taken from Kohl *et al*. (2019).

reproduce the authors' measurements. This is even more urgent given the novel nature of Machacova's and her colleagues' findings.

Recent years have brought a fast methodological transition for this field of trace gas flux measurements at plant surfaces, which has enabled many important findings. New portable analysers have replaced the traditional off-site analysis using GC, which has led to a huge increase in the spatial and temporal resolution of trace gas flux measurements (e.g. Jeffrey *et al*., 2020). However, the availability of these new analysers also poses a significant challenge to the community, as the reliability of these new methods often remains untested. Spectral interferences by VOCs emitted by the plants studied, as well as emissions from the materials used to construct chambers and the analysers themselves (e.g. from pump membranes) pose a major uncertainty in our line of research. As a community, it is important that we develop a widely accepted body of literature based upon well validated methods. As such, we provide the following list of recommendations for trace gas flux measurements at plant surfaces:

(**1**) Measurements at new systems (e.g. new tree species, new chamber design, new analysers) should be conducted with at least two independent instruments to exclude spectral interference. Ideally, measurements by GC are conducted to validate at least some flux measurements and the GC chromatograms are checked for interfering compounds.

(**2**) All measurements need to include controls with empty chambers, including all materials used for chamber construction (e.g. silicone or other chamber sealing materials) to confirm the absence of trace gas or interfering VOC emissions by chamber materials or the analyser itself.

(**3**) For measurements based on FTIR, authors should demonstrate that all major VOCs emitted by the studied plant are included in the spectral library. This may not be possible, for example if such data are not available for the studied species. In this case, FTIR should not be used for trace gas flux measurements. In addition, publications based on FTIR need to be accompanied by a list of compounds included in the spectral library and quality-of-fit criteria for the spectral deconvolution. Ideally, authors should store raw FTIR spectra and make these data available upon publication, so that researchers can reproduce the spectral deconvolution when the data are used, for example, for metastudies.

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ORCID

Lukas Kohl https://orcid.org/0000-0002-5902-9444
Markku Koskinen https://orcid.org/0000-0002-9473-6064
Mari Pihlatie https://orcid.org/0000-0001-6035-3949

Lukas Kohl[1,2]*, Markku Koskinen[1,2,3] and Mari Pihlatie[1,2,4]

[1]Department of Agricultural Sciences, University of Helsinki, Viikinkaari 9, Helsinki 00790, Finland;
[2]Institute for Atmospheric and Earth System Research (INAR), University of Helsinki, Viikinkaari 9, Helsinki 00790, Finland;
[3]Greenhouse Gases Research Group, Finnish Meteorological Institute, Erik Palménin aukio 1, Helsinki 00560, Finland;
[4]Viikki Plant Science Center (VIPS), University of Helsinki, Viikinkaari 9, Helsinki 00790, Finland
(*Author for correspondence: email lukas.kohl@helsinki.fi)

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