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Interference of volatile organic compounds on methane analysers

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Spectroscopic analysers are indispensable for studying the biogeochemical cycles of trace gases like methane (CH4). These analysers, however, are prone to spectral interferences by gas species other than the target analyte. This is especially relevant when measuring plant CH4 emissions, because these emissions are typically accompanied by volatile organic compounds (VOC) at flux rates 2-4 orders of magnitude higher than CH4 emissions.

In a recent field campaign, we measured tree stems CH4 emissions with both cavity ring-down spectroscopy (CRDS) and Fourier-transformed infrared (FTIR) spectroscopy-based instruments, which measured vastly different apparent CH4 fluxes. We hypothesised that these differences result from interferences by co-emitted VOCs, and conducted laboratory tests to quantify these interferences. In an initial series of experiments, screened for interferences of a total of 10 biogenic VOCs on five CH4 analysers (Picarro G2301, G2201i, and G4301; Los Gatos Research UGGA; Gasmet DX4015). Adding VOCs to an air stream resulted in substantial interferences (up to multiple ppm apparent CH4 per ppm VOC) on the FTIR based analyser (DX4015), whereas laser spectroscopy based analysers showed only minor (tens of ppb apparent CH4 per ppm VOC) temporary deviations from the true CH4 concentrations that lasted for <1 min. Adding reference spectra of the tested VOC to the spectral library of the FTIR analyser substantially reduced the interference of some VOCs, however, interferences were at least 10x higher compared to the CRDS based instruments.

In summary, we showed that VOC co-emissions can result in stark mismeasurements of plant CH4 emissions, and that FTIR based instruments are more prone to these interference than laser spectroscopy based instruments.