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

Lukas Kohl[1,2] , Markku Koskinen[1,2,3], Kaisa Rissanen[2,4], Iikka Haikarainen[1,2], Tatu Polvinen[1,2], Heidi Hellén[3], and Mari Pihlatie[1,2,5]

[1]Department of Agricultural Sciences, University of Helsinki, Helsinki, 00790, Finland
[2]Institute for Atmospheric and Earth System Research / Forest Sciences, Faculty of Agriculture and Forestry, University of Helsinki, Finland
[3]Finnish Meteorological Institute, PO.Box 503, 00101 Helsinki, Finland
[4]Department of Forest Sciences, University of Helsinki, Helsinki, 00790, Finland
[5]ViPS - Viikki Plant Science Center, University of Helsinki, Helsinki, 00790, Finland

Studies that quantify plant methane (4) emission rely on the accurate measurement of small changes in the mixing ratio of CH_4 that coincide with much larger changes in the mixing ratio of volatile organic compounds (VOCs). Here, we assessed if 11 commonly occurring VOCs (e.g., methanol, α- and β-pinene, Δ^3-carene) interfered with the quantitation of CH_4 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 minimal interference with laser 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 bias on FTIR-based instruments (64 - 1800 ppbv apparent CH_4 / ppmv VOC). Minor (0.7 - 126 ppbv / 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 ppbv / ppmv) and transient (<1 minute) VOC interferences on laser absorption spectroscopy based analysers. 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 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 mixing ratios, and could therefore provide a method complementary to proton-transfer-reaction mass spectrometry (PTR-MS).