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Measurements of VOC fluxes by Eddy-covariance with a PTR-Qi-TOF-MS over a mature wheat crop near Paris: Evaluation of data quality and uncertainties.

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The quantification of volatile organic compounds (VOC) fluxes exchanged by terrestrial ecosystems is of large interest because of their influence on the chemistry and composition of the atmosphere including aerosols and oxidants. Latest developments in the techniques for detecting, identifying and measuring VOC fluxes have considerably improved the abilities to get reliable estimates. Among these, the eddy-covariance (EC) methodology constitutes the most direct approach, and relies on both well-established principles (Aubinet et al. 2000) and a sound continuously worldwide improving experience. The combination of the EC methodology with the latest proton-transfer-reaction mass spectrometer (PTR-MS) device, the PTR-Qi-TOF-MS, which allows the identification and quantification of more than 500 VOC at high frequency, now provides a very powerful and precise tool for an accurate quantification of VOC fluxes on various types of terrestrial ecosystems. The complexity of the whole methodology however demands that several data quality requirements are fulfilled.

VOC fluxes were measured by EC with a PTR-Qi-TOF-MS (national instrument within the ANAEE-France framework) for one month and a half over a mature wheat crop near Paris (FR-GRI ICOS site). Most important emissions (by descending order) were observed from detected compounds with mass-over-charge (m/z) ratios of 33.033 (methanol), 45.033 (acetaldehyde), 93.033 (not identified yet), 59.049 (acetone), and 63.026 (dimethyl sulfide or DMS). Emissions from higher-mass compounds, which might be due to pesticide applications at the beginning of our observation period, were also detected. Some compounds were also seen to deposit (e.g. m/z 47.013, 71.085, 75.044, 83.05) while others exhibited bidirectional fluxes (e.g. m/z 57.07, 69.07). Before analyzing VOC flux responses to meteorological and crop development drivers, a data quality check was performed which included (i) uncertainty analysis of mass and concentration calibration, (ii) determination of fragmentation patterns and (iii) of lag time high-frequency losses for all ions that showed a flux, and (iv) the determination of the flux random uncertainties and of the limit of detection.