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Evaluation of an on-line methodology for measuring volatile organic compounds (VOC) fluxes by eddy-covariance with a PTR-TOF-Qi-MS

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Field scale flux measurements of volatile organic compounds (VOC) are essential for improving our knowledge of VOC emissions from ecosystems. Many VOCs are emitted from and deposited to ecosystems. Especially less known, are crops which represent more than 50% of French terrestrial surfaces. In this study, we evaluate a new on-line methodology for measuring VOC fluxes by Eddy Covariance with a PTR-Qi-TOF-MS. Measurements were performed at the ICOS FR-GRI site over a crop using a 30 m long high flow rate sampling line and an ultrasonic anemometer. A Labview program was specially designed for acquisition and on-line covariance calculation: Whole mass spectra (∼240000 channels) were acquired on-line at 10 Hz and stored in a temporary memory. Every 5 minutes, the spectra were mass-calibrated and normalized by the primary ion peak integral at 10 Hz. The mass spectra peaks were then retrieved from the 5-min averaged spectra by withdrawing the baseline, determining the resolution and using a multiple-peak detection algorithm. In order to optimize the peak detection algorithm for the covariance, we determined the covariances as the integrals of the peaks of the vertical-air-velocity-fluctuation weighed-averaged-spectra. In other terms, we calculate <w'(t)Sp'(t-lag)>, were w is the vertical component of the air velocity, Sp is the spectra, t is time, lag is the decorrelation lag time and <.> denotes an average. The lag time was determined as the decorrelation time between w and the primary ion (at mass 21.022) which integrates the contribution of all reactions of VOC and water with the primary ion. Our algorithm was evaluated by comparing the exchange velocity of water vapor measured by an open path absorption spectroscopy instrument and the water cluster measured with the PTRQi-TOF-MS. The influence of the algorithm parameters and lag determination is discussed. This study was supported by the ADEME-CORTEA COV3ER project (http://www6.inra.fr/cov3er).