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Field and laboratory study on atmospheric δ^{13}C-CO_2 using FTIR spectroscopy

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The ^{13}C/^{12}C ratio of atmospheric CO_2 (δ^{13}C-CO_2) is a powerful tool to quantify CO_2 flux strength of different ecosystem compartments. To date, the majority of CO_2 isotope studies have required air sample collection at remote locations, followed by laboratory analysis with isotope ratio mass spectrometry (IRMS), which limits the number and frequency of measurements [1]. In our study we demonstrate the utility of Fourier transform infrared spectroscopy (FTIR) for online analysis of δ^{13}C-CO_2 in ambient air. Quantification relies on a novel calibration strategy based on a robust partial least squares (PLS) algorithm in combination with a set of multi-component standard spectra [2]. Furthermore, the instrumental set-up has significantly been improved to stabilize gas temperature and pressure. Thus in the laboratory we achieved an average accuracy for δ^{13}C-CO_2 of 0.4 per mil and a precision of 0.15 per mil. The ability of the instrument to measure δ^{13}C-CO_2 was tested outdoors in a grassland and compared to standard laboratory-based MS measurements made on field-collected flask samples. The average difference for δ^{13}C-CO_2 between FTIR and IRMS after removal of two outliers was 0.5 per mil (n = 83). A very good agreement was found for the carbon isotope content of respired CO_2 ($\delta^{13}C_R$) determined by either FTIR spectroscopy or IRMS. Besides δ_{13}C-CO_2 and CO_2, other important trace gases, such as CO, N_2O and CH_4 were analyzed by FTIR with high accuracy and precision.

[1] E. Kerstel, in P. de Groot (Eds.), Handbook of Stable Isotope Analytical Techniques, Vol. I, Elsevier, Amsterdam, 2004, chapter 34.

[2] J. Mohn, R. A. Werner, B. B. and L. Emmenegger, J. Mol. Struct., (accepted) (2007).