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Application of a quantum cascade laser based spectrometer for realtime δ^{13}C and δ^{18}O measurements of soil-respired CO_2

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Stable isotope analysis is a powerful tool to assess the sources of CO_2 effluxes from soils. Keeling plots are frequently used to determine δ^{13}C and δ^{18}O of soil-respired CO_2 using closed soil chambers. Uncertainties, however, still exist whether there is a strict linearity - as required for Keeling plots - between the isotope ratio and 1/CO_2 throughout the CO_2 accumulation in the chamber, because in most studies only a few gas samples were analyzed in the laboratory using isotope ratio mass spectrometry (IRMS).

In a beech forest of the Swiss Jura, we applied a recently developed quantum cascade laser based spectrometer (Aerodyne Inc. and EMPA) to investigate ^{13}C and ^{18}O dynamics of CO_2 in a closed chamber system placed on soils with a ^{13}C labelled litter layer. A recirculation sampling scheme permitted the realtime monitoring of the CO_2 isotope ratios in the chamber headspace with a sampling frequency of one second. Within two days we performed 90 chamber measurements with 20 minutes sampling time, each resulting in Keeling plots of 1200 data points.

At first glance, the linearity of the Keeling plots was ensured as indicated by ordinary least square fits with R^2 values of 0.96 - 0.99 and standard errors of the intercept $<0.1‰$. The high time resolution of the instrument, however, allowed us to identify the following: (i) the δ^{13}C of the soil-respired CO_2 ($\delta^{13}C_{\mathrm{resp}}$) estimated from moving windows of 400 data points increased by 1.9‰ when the CO_2 accumulation exceeded 300 ppm. (ii) The $^{13}CO_2$ started to oscillate during flux measurements, but not the $^{12}C^{16}O_2$ and the $^{12}C^{16}O^{18}O$. (iii) The δ^{18}O- Keeling plots showed a curved trend, which significantly differed from the linear correlation, and (iv) over two observation days, $\delta^{13}C_{\mathrm{resp}}$ and $\delta^{18}O_{\mathrm{resp}}$ varied by 2 - 5.5‰ and did not follow a daily pattern.

In this presentation we will discuss our observations and show how realtime measurements can improve estimates of $\delta^{13}C_{\mathrm{resp}}$ and $\delta^{18}O_{\mathrm{resp}}$.