



Application of a laser-based spectrometer for continuous in situ measurements of stable isotopes of soil CO₂ in calcareous and acidic soils

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Abstract. The short-term dynamics of carbon and water fluxes across the soil–plant–atmosphere continuum are still not fully understood. One important constraint is the lack of methodologies that enable simultaneous measurements of soil CO₂ concentration and respective isotopic composition at a high temporal resolution for longer periods of time. $\delta^{13}\text{C}$ of soil CO₂ can be used to derive information on the origin and physiological history of carbon, and $\delta^{18}\text{O}$ in soil CO₂ aids in inferring the interaction between CO₂ and soil water. We established a real-time method for measuring soil CO₂ concentration, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values across a soil profile at higher temporal resolutions (0.05–0.1 Hz) using an off-axis integrated cavity output spectroscopy (OA-ICOS). We also developed a calibration method correcting for the sensitivity of the device against concentration-dependent shifts in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values under highly varying CO₂ concentration. The deviations of measured data were modelled, and a mathematical correction model was developed and applied for correcting the shift. By coupling an OA-ICOS with hydrophobic but gas-permeable membranes placed at different depths in acidic and calcareous soils, we investigated the contribution of abiotic and biotic components to total soil CO₂ release. We found that in the calcareous Gleysol, CO₂ originating from carbonate dissolution contributed to the total soil CO₂ concentration at detectable degrees, potentially due to CO₂ evasion from groundwater. The ^{13}C -CO₂ of topsoil at the calcareous soil site was found reflect $\delta^{13}\text{C}$ values of atmospheric CO₂, and the $\delta^{13}\text{C}$ of topsoil CO₂ at the acidic soil site was representative of the biological respiratory processes. $\delta^{18}\text{O}$ values of CO₂ in both sites reflected the $\delta^{18}\text{O}$ of soil water across most of the depth profile, except for the 80 cm depth at the calcareous site where a relative enrichment in ^{18}O was observed.

1 Introduction

Global fluxes of CO₂ and H₂O are two major driving forces controlling earth's climatic systems. To understand the prevailing climatic conditions and predict climate change, accurate monitoring and modelling of these fluxes are essential (Barthel et al., 2014; Harwood et al., 1999; Schär et

al., 2004). Soil respiration, the CO₂ flux released from the soil surface to the atmosphere as a result of microbial and root respiration (heterotrophic and autotrophic), is the second largest terrestrial carbon flux (Bond-Lamberty and Thomson, 2010). The long-term dynamics of CO₂ release on a seasonal scale are reasonably well understood (Satakhun et al., 2013), whereas less information on CO₂ dynamics and iso-

topic composition is available for short-term variations on a diurnal scale (Werner and Gessler, 2011). The lack of a proper understanding of the diurnal fluctuations in soil CO₂ release might introduce uncertainty in estimating the soil carbon budget and the CO₂ fluxes to the atmosphere. The isotopic composition of soil CO₂ and its diel fluctuation can be a critical parameter for the partitioning of ecosystem gas exchange into its components (Bowling et al., 2003; Mortazavi et al., 2004) and for disentangling plant and ecosystem processes (Werner and Gessler, 2011). By assessing the $\delta^{13}\text{C}$ of soil CO₂, it is possible to identify the source for CO₂ (Kuzaykov, 2006) and the coupling between photosynthesis and soil respiration when taking into account post-photosynthetic isotope fractionation (Werner et al., 2012; Wingate et al., 2010). $\delta^{13}\text{C}$ soil CO₂ reflects, however, not only microbial and root respiration but also abiotic sources from carbonate weathering (Schindlbacher et al., 2015).

Soil water imprints its $\delta^{18}\text{O}$ signature on soil CO₂ as a result of isotope exchange between H₂O and CO₂ (aqueous). The oxygen isotopic exchange between CO₂ and soil water is catalysed by microbial carbonic anhydrase (Sperber et al., 2015; Wingate et al., 2009). Thus, soil CO₂ can give information on the isotopic composition of both soil water resources and carbon sources. The oxygen isotope composition of plant-derived CO₂ is both a tracer of photosynthetic and respiratory CO₂ and gives additional quantitative information on the water cycle in terrestrial ecosystems (Francey and Tans, 1987). To better interpret the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ signals of atmospheric CO₂, the isotopic composition and its variability in the different sources need to be better understood (Werner et al., 2012; Wingate et al., 2010).

The conventional method for estimating the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of soil CO₂ efflux is by using two end-member mixing models of atmospheric CO₂ and CO₂ produced in the soil (Keeling, 1958). The conventional methods for sampling soil produced CO₂ are chamber-based (Bertolini et al., 2006; Torn et al., 2003), “mini-tower” (Kayler et al., 2010; Mortazavi et al., 2004), and soil-gas-well-based (Breecker and Sharp, 2008; Oerter and Amundson, 2016) methods. In conventional methods, air sampling is done at specific time intervals, and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ are analysed using isotope ratio mass spectrometry (IRMS; Ohlsson et al., 2005). Such offline methods have several disadvantages, like high sampling costs, excessive time consumption for sampling and analysis, and increased sampling error and low temporal resolution. Kammer et al. (2011), showed how error prone the conventional methods could be while calculating $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ (up to several per mil when using chamber and mini-tower-based methods; Kammer et al., 2011). In chamber-based systems, non-steady-state conditions may arise within the chamber due to increased CO₂ concentrations, which in turn hinders the diffusion of ¹²CO₂ more strongly than that of heavier ¹³CO₂ (Risk and Kellman, 2008). Moreover, it has been found that $\delta^{18}\text{O}$ of the CO₂ inside a chamber is significantly influenced by the $\delta^{18}\text{O}$ of the surface soil water, as an equilibrium iso-

topic exchange happens during the upward diffusive movement of soil CO₂ (Mortazavi et al., 2004). The advent of laser-based isotope spectroscopy has enabled cost-effective, simple, and high precision real-time measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ (Kammer et al., 2011; Kerstel and Gianfrani, 2008). This technique opened up new possibilities for faster and reliable measurements of stable isotopes in situ, based on the principle of light absorption, using laser beams of distinct wavelengths in the near- and mid-infrared range (Bowling et al., 2003). Recently, several high-frequency online measurements of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$, of soil CO₂ and ²H, and of the ¹⁸O of soil water vapour across soil depth profiles were reported by coupling either hydrophobic but gas-permeable membranes (installed at different depths in soil) or automated chamber systems with laser spectrometers (Bowling et al., 2015; Jochheim et al., 2018; Stumpp et al., 2018). Such approaches enable detection of vertical concentration profiles, temporal dynamics of soil CO₂ concentration, and the isotopic signature of soil CO₂ across different soil layers, thus aiding in identifying and quantifying various sources of CO₂ across the depth profile.

In 1988, O’Keefe and Deacon introduced cavity ring-down spectroscopy (CRDS) for measuring the isotopic ratio of different gaseous species based on laser spectrometry (O’Keefe and Deacon, 1988). With the laser-based spectrometry techniques, measuring sensitivities up to parts per trillion (ppt) concentrations is achieved (von Basum et al., 2004; Peltola et al., 2012). In CRDS, the rate of change in the absorbed radiation of the laser light that is temporarily “trapped” within a highly reflective optical cavity is determined. This is achieved using resonant coupling of a laser beam to the optical cavity and active locking of laser frequency to cavity length (Parameswaran et al., 2009). Another well-established technique similar to CRDS is off-axis integrated cavity output spectroscopy (OA-ICOS). It is based on directing narrowband and continuous-wave lasers in an off-axis configuration to the optical cavity (Baer et al., 2002).

Even though OA-ICOS can measure concentration and isotope signature of various gaseous species at a high temporal resolution, we found pronounced deviations in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements from the absolute values when measured under changing CO₂ concentrations. So far, to our knowledge, no study detailing the calibration process of OA-ICOS CO₂ analysers correcting for fluctuations of both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values under varying CO₂ concentrations has been made available. Most of the OA-ICOS CO₂ analysers are built for working under stable CO₂ concentrations, so periodical calibration against in-house gas standards at a particular concentration is sufficient. However, as there are pronounced gradients in CO₂ levels in soils (Maier and Schack-Kirchner, 2014), CO₂-concentration-dependent shifts in measured isotopic values have to be addressed and corrected. Such calibration is, however, also relevant for any other OA-ICOS application with varying levels of CO₂ (e.g. in chamber measurements). Hence the first part of this work comprises the

establishment of a calibration method for OA-ICOS. The second part describes a method for online measurement of CO₂ concentrations and stable carbon and oxygen isotope composition of CO₂ in different soil depths by coupling OA-ICOS with gas-permeable hydrophobic tubes (membrane tubes, Accurel®). The use of these tubes for measuring soil CO₂ concentration (Gut et al., 1998) and the $\delta^{13}\text{C}$ of soil CO₂ (Parent et al., 2013) has already been established, but the coupling to an OA-ICOS system has not been performed, yet.

We evaluated our measurement system by assessing and comparing the concentration of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of soil CO₂ for a calcareous and an acidic soil system. The primary foci of this study are to (1) introduce OA-ICOS in online soil CO₂ concentration and isotopic measurements, (2) calibrate the OA-ICOS to render it usable for isotopic analysis carried out under varying CO₂ concentrations, and (3) analyse the dynamics of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of soil CO₂ at different soil depths in different soil types at a higher temporal resolution.

2 Materials and methods

2.1 Instrumentation

The concentration of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of CO₂ were measured with an OA-ICOS, as described in detail by Baer et al. (2002) and Jost et al. (2006). In this study, we used an OA-ICOS, (LGR CCIA 36-d) manufactured by Los Gatos Research Ltd in San Francisco, USA. The LGR CCIA 36-d measures CO₂ concentration and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values at a frequency up to 1 Hz. The operational CO₂ concentration range was 400 to 25 000 ppm. The operating temperature range was +10–+35 °C, and the sample temperature range (gas temperature) was between –20 and 50 °C. The recommended inlet pressure was < 0.0689 MPa. The multiport inlet unit (MIU), an optional design that comes along with LGR CCIA 36-d, had a manifold of eight digitally controlled inlet ports and one outlet port. It presented the user with an option of measuring eight different CO₂ samples at the desired time interval. Three standard gases with distinct $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were used for calibration in this study (see Table S1 in the Supplement). The standard gases used in this study were analysed for absolute concentration and respective $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. δ values are expressed based on Vienna Pee Dee Belemnite (VPDB) CO₂ scale and were determined by high precision IRMS analysis.

2.2 Calibration set-up and protocol

We developed a two-step calibration procedure to (a) correct for concentration-dependent errors in isotopic data measurements and (b) correct for deviations in measured δ values from absolute values due to the offset (other than concentration-dependent error) introduced by the laser spectrometer. Also, we used Allan variance curves for determining the time interval to average the data (Nelson et al., 2008)

in order to achieve the highest precision that can be offered by the LGR CCIA 36-d (Allan et al., 1997).

The first part of our calibration methodology was developed to correct for the concentration-dependent error observed in preliminary studies for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values measured using OA-ICOS. Such a calibration protocol was used in addition to the routine three-point calibration performed with in-house CO₂ gas standards of known $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. We developed a CO₂ dilution set-up (see Fig. 1) in which each of the three CO₂ standard gases was diluted with synthetic CO₂-free air (synthetic air) to different CO₂ concentrations. By applying a dilution series, we identified the deviation of the measured (OA-ICOS) from the absolute (IRMS) $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values depending on CO₂ concentration (see Fig. 4). The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of our in-house calibration gas standards were measured via cryoextraction and dual-inlet IRMS. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of the standard gases (see Table S1) across a wide range of CO₂ concentrations are measured using OA-ICOS. The deviation of the measured $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ from absolute values with respect to changing CO₂ concentrations was mathematically modelled and later used for data correction (see Fig. 5). A standard three-point calibration was then applied to correcting for concentration-dependent errors (see Fig. 7). The standards used covered a wide range of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, including the values observed in the field of application.

Standard gases were released to a mass flow controller (ANALYT-MTC, series 358, MFC1) after passing through a pressure controller valve (see Fig. 1) with safety bypass (TESCOM, D43376-AR-00-X1-S, version 5). A Swagelok filter, (Stainless Steel All-Welded In-Line Filter; Swagelok, SS-4FWS-05, F1) was installed at the inlet of the flow controller (ANALYT-MTC, series 358, MFC1). Synthetic air was released and passed to another flow controller (ANALYT-MTC, series 358, MFC2) through a Swagelok filter (F2 in Fig. 1). CO₂ and synthetic air leaving the flow controllers (MFC1 and MFC2 respectively) were then mixed and drawn through a Teflon tube (P8) with a 6.35 mm outer diameter (OD), which was kept in a gas thermostat unit (see Fig. 1). The thermostat unit contained (a) a thermostat-controlled water bath (Kottermann, 3082) and (b) an Isotherm flask containing liquid nitrogen. The water bath was used to raise the temperature above room temperature and also to bring the temperature down to +5 °C by placing ice packs in the water bath. To reach low temperatures (–20 °C), we immersed the tubes in the isotherm flask filled with liquid N₂. Leaving the thermostat unit, the gas was directed to the multiport inlet unit of the OA-ICOS. By using the thermostat unit, we introduced a shift in the reference gas temperature, and the aim was to test the temperature sensitivity of the OA-ICOS in measuring $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values. The third CO₂ standard gas (which is used for validation) was produced by mixing the other two gas standards in equal molar proportions in a 10 L volume plastic bag with an inner aluminum foil coating and welded seams

In situ measurements in an acidic soil were conducted by the end of July 2014 in the model ecosystem facility (MODOEK) of the Swiss Federal Research Institute WSL in Birmensdorf, Switzerland (47°21'48" N, 8°27'23" E; 545 m a.s.l.). The MODOEK facility comprises 16 model ecosystems, split below ground into two lysimeters with an area of 3 m² and a depth of 150 cm. The lysimeters used for the present study were filled with acidic (Haplic Alisol) forest soil IUSS (2014) and planted with young beech trees (Arend et al., 2016). The soil pH was 4.0, with a total SOC content of 0.8 % (Kuster et al., 2013).

2.4 Experimental set-up

The OA-ICOS was connected to gas-permeable, hydrophobic membrane tubes (Accurel® tubing, 8 mm outer diameter) of 2 m length, placed horizontally in the soil at different depths. Tubes were laid in six different depths (4, 8, 12, 17, 35, and 80 cm) for calcareous soil and three depths (10, 30, and 60 cm) for acidic soil.

Technical details of the measurement set-up are shown in Fig. 2. Both ends of the membrane tubes were extended vertically upwards, reaching the soil top by connecting them to gas impermeable Synflex® tubing (8 mm OD) using Swagelok tube fitting union (Swagelok: SS-8M0-6, 8 mm tube OD). One end of the tubing system was connected to a solenoid switching valve (Bibus: MX-758.8E3C3KK), by using a stainless-steel reducing union (Swagelok: SS-8M0-6-6M), to the outlet of the LGR CCIA 36-d by using 6.35 mm (OD) Teflon tubing. The other end was connected via the multiport inlet unit to the gas inlet of the LGR CCIA 36-d.

This way, a loop was created in which the soil CO₂ drawn into the OA-ICOS was circulated back through the tubes and in and out of the OA-ICOS and measured until a steady state was reached. We experienced no drop in cavity pressure while maintaining a closed loop (see Fig. S2). Each depth was selected and continuously measured for 6 min at specified time intervals by switching to defined depths at the multiport inlet unit and also at the solenoid valve.

3 Results and discussion

3.1 Instrument calibration and correction

The highest level of precision obtained for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements at the maximum measuring frequency (1 Hz) was determined by using Allan deviation curves (see Fig. 3). The maximum precision of 0.022 ‰ for $\delta^{13}\text{C}$ was obtained when the data were averaged over 256 s, and the maximum for $\delta^{18}\text{O}$, 0.077 ‰, was obtained for the same averaging interval as for $\delta^{13}\text{C}$.

To correct for CO₂ concentration-dependent errors in raw $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ data, we analysed data obtained from the OA-ICOS to determine the sensitivity of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements against changing concentrations of CO₂. We observed

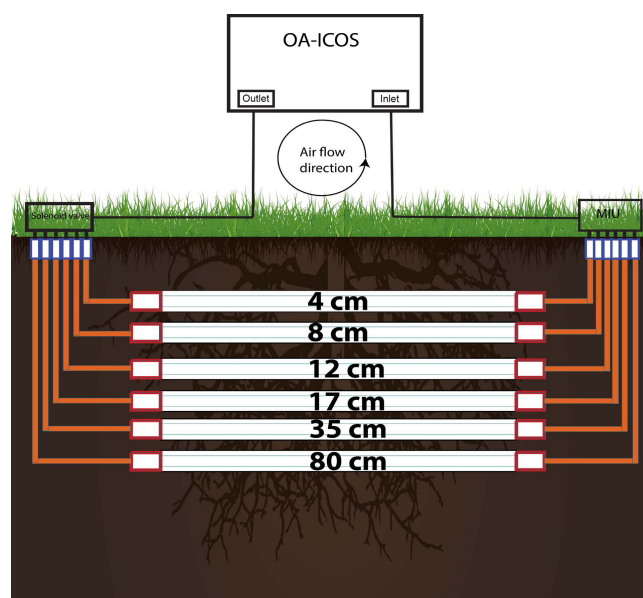


Figure 2. Installation made for soil air CO₂ (ppm), $\delta^{13}\text{C}$ -CO₂ and $\delta^{18}\text{O}$ -CO₂ measurements using off-axis integrated cavity output spectrometer (OA-ICOS). Hydrophobic membrane tubing was installed horizontally in soil at different depths. MIU: multiport inlet unit.

a specific pattern of deviance in the measured isotopic data from the absolute values (both for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) across CO₂ concentration ranging from 25 000 to 400 ppm (see Fig. 4). Uncalibrated $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements showed a standard deviation of 6.44 ‰ and 6.80 ‰ respectively, when measured under changing CO₂ concentrations.

The dependency of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values on the CO₂ concentration was compensated by using a non-linear model. The deviations (Diff- δ) of the measured delta values ($\delta_{(\text{OA-ICOS})}$) from the absolute value of the standard gas ($\delta_{(\text{IRMS})}$) at different concentrations of CO₂ were calculated ($\text{Diff-}\delta = \delta_{(\text{OA-ICOS})} - \delta_{(\text{IRMS})}$). Several mathematical models were then fitted to Diff- δ as a function of changing CO₂ concentration (see Fig. 5). The mathematical model with the best fit for Diff- δ data was selected using the corrected Akaike information criterion (AIC_C; Glatting et al., 2007; Hurvich and Tsai, 1989; Yamaoka et al., 1978). The non-linear model fits applied for Diff- $\delta^{13}\text{C}$ and Diff- $\delta^{18}\text{O}$ measurements are given in Tables 1 and 2, respectively. For Diff- $\delta^{13}\text{C}$, a three-parameter exponential model fitted best with $r^2 = 0.99$ (see Table 3 for the values of the parameters; see Fig. S3a for model residuals), and a three-parameter power function model (see Table 2) with $r^2 = 0.99$ showed the best fit for Diff- $\delta^{18}\text{O}$ (see Table 3 for the values of the parameters; see Fig. S3b for model residuals). The best fit was then introduced into the measured isotopic data ($\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) and corrected for concentration-dependent errors (see Fig. 6). After correction, the standard deviation of $\delta^{13}\text{C}$ was reduced

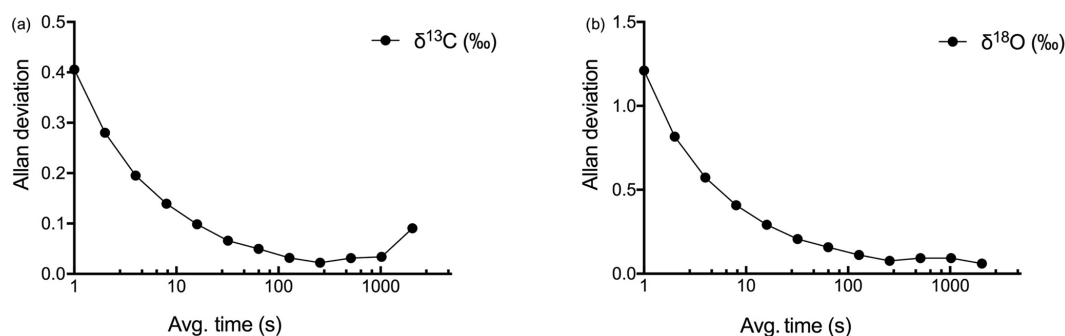


Figure 3. Allan deviation curve for $\delta^{13}\text{C}$ (a) and $\delta^{18}\text{O}$ (b) measurements by OA-ICOS CO₂ carbon isotope analyser (LGR CCIA-36d).

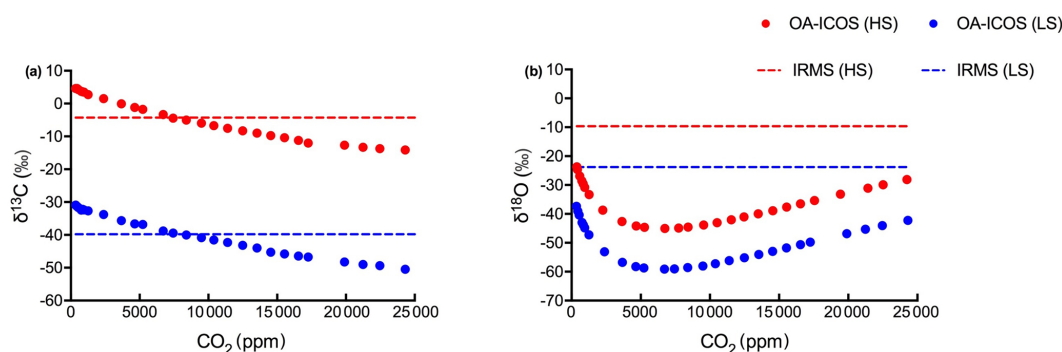


Figure 4. Variability observed in (a) $\delta^{13}\text{C}$ and (b) $\delta^{18}\text{O}$ measurements using OA-ICOS before calibration. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measured using OA-ICOS for heavy standard and light standard are shown as red and blue circles respectively. Actual $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values reported after measuring by IRMS for heavy standard and light standard are shown as red and blue dashed lines respectively.

to 0.08‰, and the deviation of $\delta^{18}\text{O}$ to 0.09‰, for all measurements across the whole CO₂ concentration range.

After correcting the measured $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values for the CO₂ concentration-dependent deviations, a three-point calibration (Sturm et al., 2012) was made by generating linear regressions with the concentration-corrected $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values against absolute $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values (see Fig. 7; see Fig. S4 for linear regression residuals). Using the linear regression lines, we were able to measure the validation gas standard, with standard deviations of 0.0826‰ for $\delta^{13}\text{C}$ and 0.0941‰ for $\delta^{18}\text{O}$.

For the LGR CCIA 36-d, we found that routine calibration (correction for concentration-dependent error plus three-point calibration) was necessary for obtaining the required accuracy, in particular under fluctuating CO₂ concentrations. The LGR CCIA-36d offers an option for calibration against a single standard, a feature which was already in place in a predecessor model (CCIA DLT-100; Guillon et al., 2012). This internal calibration is sufficient when LGR CCIA-36d is operated only under stable CO₂ concentrations. To correct for the concentration dependency, we introduced mathematical model fits, which corrected for the deviation pattern found for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$. We assume that these deviations are instrument specific and that the fitting parameters need to be adjusted for every single device. Experiments conducted

to investigate the influence of external temperature fluctuations on OA-ICOS measurements did not show any significant changes in the temperature inside the optical cavity of the OA-ICOS (see Fig. S1). The previous version of the Los Gatos CCIA was strongly influenced by temperature fluctuations during sampling (Guillon et al., 2012). The lack of temperature dependency as observed here with the most recent model can be mostly due to the heavy insulation provided with the system, which was not found in the older models.

Guillon et al. (2012) found a linear correlation between CO₂ concentration and respective stable isotope signatures with a previous version of the Los Gatos CCIA CO₂ stable isotope analyser. In our experiments with the OA-ICOS, the best fitting correlations between CO₂ concentration and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements were exponential and power functions, respectively. We assume that measurement accuracy is influenced by the number of CO₂ molecules present inside the laser cavity of the particular laser spectrometer, as we observed large standard deviation in isotopic measurements at lower CO₂ concentrations. This behaviour of an OA-ICOS can be expected, as it functions by sweeping the laser along an absorption spectrum, measuring the energy transmitted after passing through the sample. Therefore, energy transmitted is proportional to the gas concentration in the cavity. The laser absorbance is then determined by normalising against a

Table 1. Correction factor models are fitted for Diff- $\delta^{13}\text{C}$, DF (degrees of freedom), AIC_C (Akaike information criterion), and [CO₂] CO₂ concentration in ppm.

Model fit	Equation	R^2	AIC _C	DF
Exponential	$\text{Diff-}\delta^{13}\text{C} = a \times (b - \exp(-c \times [\text{CO}_2]))$	0.99	-294.6	54
Polynomial	$\text{Diff-}\delta^{13}\text{C} = a + (b \times [\text{CO}_2]) + (c/[\text{CO}_2]^2)$	0.98	-27.56	54
Logarithmic	$\text{Diff-}\delta^{13}\text{C} = a + b \times \ln([\text{CO}_2])$	0.89	91.68	55
LOWESS	–	0.99	-170.24	54

Table 2. Correction factor models are fitted for Diff- $\delta^{18}\text{O}$, DF (degrees of freedom), AIC_C (Akaike information criterion), and [CO₂] CO₂ concentration in ppm.

Model fit	Equation	R^2	AIC _C	DF
Power	$\text{Diff-}\delta^{18}\text{O} = a \times (b^{[\text{CO}_2]}) \times ([\text{CO}_2]^c)$	0.99	-337.04	51
Polynomial	$\text{Diff-}\delta^{18}\text{O} = (a + b \times x) / (1 + c \times [\text{CO}_2] + d \times [\text{CO}_2]^2)$	0.98	-19.34	50
Steinhart–Hart	$\text{Diff-}\delta^{18}\text{O} = 1/a + (b \times \ln[\text{CO}_2]) + (c \times (\ln[\text{CO}_2])^3)$	0.96	29.77	51
LOWESS	–	0.78	128.66	51

Table 3. Parameter values for correction factor model fit for Diff- $\delta^{13}\text{C}$ and Diff- $\delta^{18}\text{O}$.

Parameter	Value	SE	95 % confidence
$a^{13}\text{C}$	31.007	0.2149	30.57–31.43
$b^{13}\text{C}$	0.713	0.002376	0.708995–0.718522
$c^{13}\text{C}$	0.000043	0.000000	0.000042–0.000043
$a^{18}\text{O}$	0.85	0.003	0.8455–0.8576
$b^{18}\text{O}$	0.99	0.00	0.999928–0.9999283
$c^{18}\text{O}$	0.477	0.0047	0.476871–0.478767

reference signal, finally calculating the concentration of the sample measured by integrating the whole spectrum of absorbance (O’Keefe et al., 1999).

3.2 Variation in soil CO₂ concentration, carbon, and oxygen isotope values

Figures 9 and 10 show the CO₂ concentration and the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements of soil CO₂ in the calcareous as well as in the acidic soil across the soil profile with a sub-daily resolution and as averages for the day, respectively. We observed an increase in the CO₂ concentration across the soil depth profile for both the calcareous and the acidic soil. Moreover, there were rather contrasting $\delta^{13}\text{C}$ values across the profile for the two soil types. In the calcareous soil, CO₂ was relatively enriched in ^{13}C in the surface soil (4 cm) as compared to the 8 cm depth. Below 8 cm down to 80 cm depth, we found an increase in $\delta^{13}\text{C}$ values. At 80 cm depth, the $\delta^{13}\text{C}$ in soil CO₂ ranged between -7.15‰ and -3.35‰ (see Fig. 9), with a daily average of $-6.19 \pm 1.45\text{‰}$

(see Fig. 10), hence being clearly above atmospheric values ($\approx -8.0\text{‰}$). For $\delta^{18}\text{O}$ values of calcareous soil, the depth profile showed no specific pattern, except for the $\delta^{18}\text{O}$ values at 80 cm depth, which were found to be less negative than the values at the other depths. The $\delta^{18}\text{O}$ value in the top 4 cm was found to be slightly more enriched than the 8 cm depth, and between 8–35 cm, $\delta^{18}\text{O}$ values showed little variation relative to each other. For the sub-daily measurements, we observed a sharp decline in $\delta^{18}\text{O}$ values at around 02:00 CET, which is also observed but less pronounced for the $\delta^{13}\text{C}$ signal. We assume that the reason for such aberrant values is a technical issue rather than a biological process. It could be due to the fact that the internal pump in the OA-ICOS was not taking an adequate amount of gas into the optical cavity, thereby creating a negative pressure inside the cavity resulting in the observed aberrant values. The patterns observed for the $\delta^{13}\text{C}$ values of CO₂ in the calcareous soil with ^{13}C enrichment in deeper soil layers can be explained by a substantial contribution of CO₂ from abiotic origin to total soil CO₂ release as a result of carbonate weathering and subsequent outgassing from soil water (Schindlbacher et al., 2015). According to Cerling (1984), the distinct oxygen and carbon isotopic composition of soil carbonate depends primarily on the isotopic signature of meteoric water and on the proportion of C₄ biomass present at the time of carbonate formation (Cerling, 1984) but also on numerous other factors that determine the ^{13}C value of soil CO₂. CO₂ released as a result from carbonates in calcareous soil site have a distinct $\delta^{13}\text{C}$ value of -9.3 (mean value across soil profile 0–80 cm depth; Fig. 8c), while CO₂ released during biological respiratory processes has $\delta^{13}\text{C}$ values around -24‰ , as observed in the acidic soil (Fig. 10e). The $\delta^{13}\text{C}$ values of soil

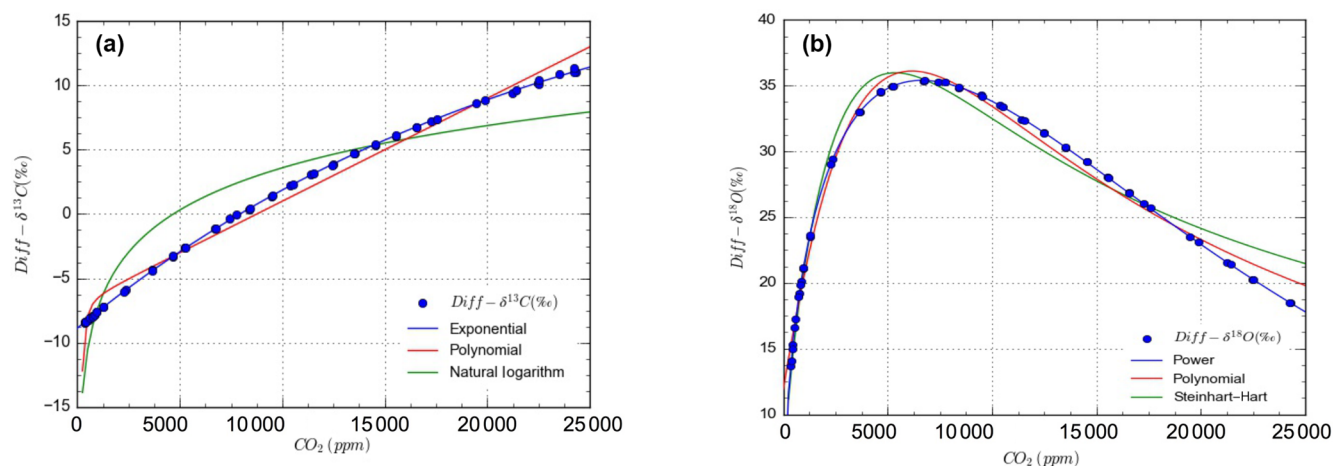


Figure 5. Mathematical models for concentration dependent drift in OA-ICOS measurements of stable isotopes of carbon (a) and oxygen (b) in CO₂ from IRMS measurements. Blue circles show Diff- $\delta^{13}\text{C}$ (a) and Diff- $\delta^{18}\text{O}$ (b) data points, and lines represent different mathematical models fitted on the measured data.

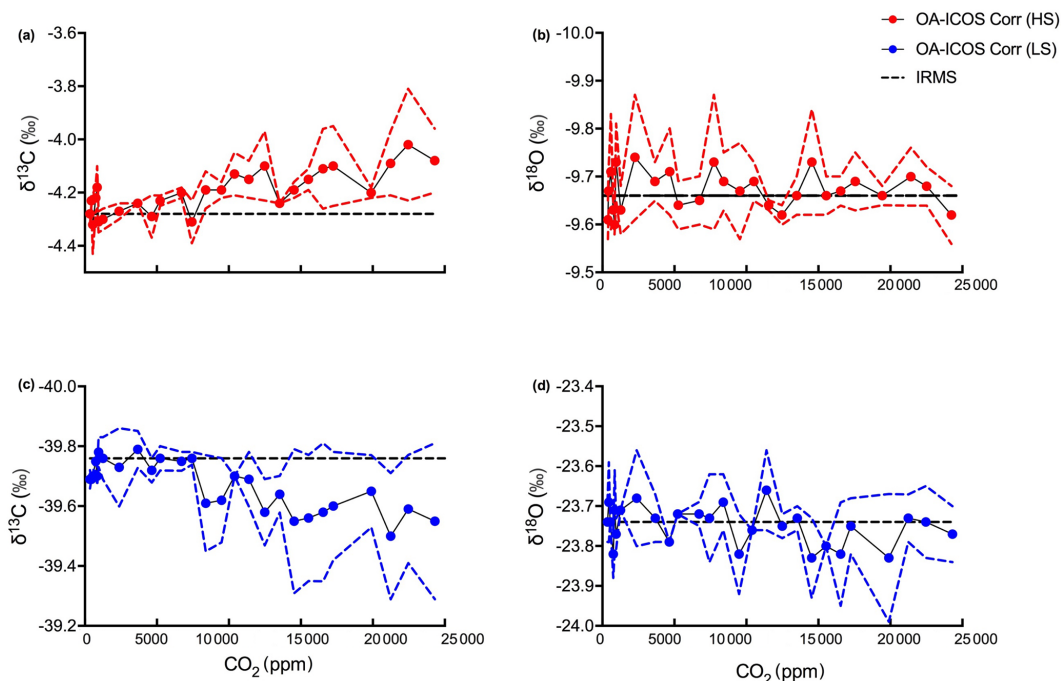


Figure 6. Corrected (a, c) $\delta^{13}\text{C}$ and (b, d) $\delta^{18}\text{O}$ measurements by OA-ICOS CO₂ carbon isotope analyser. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measured for heavy standard and light standard are shown as red and blue circles respectively. Actual $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values reported after measuring by IRMS are shown as black dashed lines, and 95 % confidence intervals are shown as coloured dashed lines, respectively.

CO₂ observed in the deepest soil layer in the calcareous soil site most likely indicate the presence of carbonate sources of a pedogenic and geologic origin. Even though the contribution of CO₂ from abiotic sources to soil CO₂ is often considered to be low, several studies have reported significant proportions ranging between (10 %–60 %), emanating from abiotic sources (Emmerich, 2003; Plestenjak et al., 2012; Ramnarine et al., 2012; Serrano-Ortiz et al., 2010; Steven-

son and Verburg, 2006; Tamir et al., 2011). Bowen and Beerling (2004) showed that isotope effects associated with soil organic matter (SOM) decomposition can cause a strong gradient in δ values of soil organic matter with depth but are not always reflected in the $\delta^{13}\text{C}$ values of soil CO₂. We have measured soil samples for bulk soil $\delta^{13}\text{C}$, carbonate $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ values and have also determined the percentage of total carbon in the soil across a depth profile of (0–80 cm; see

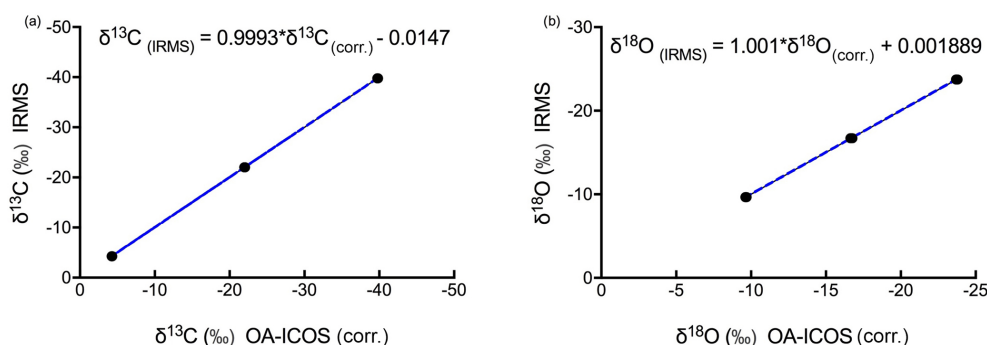


Figure 7. Three-point calibration lines for (a) $\delta^{13}\text{C}$ and (b) $\delta^{18}\text{O}$ measurements using OA-ICOS with 95 % confidence interval.

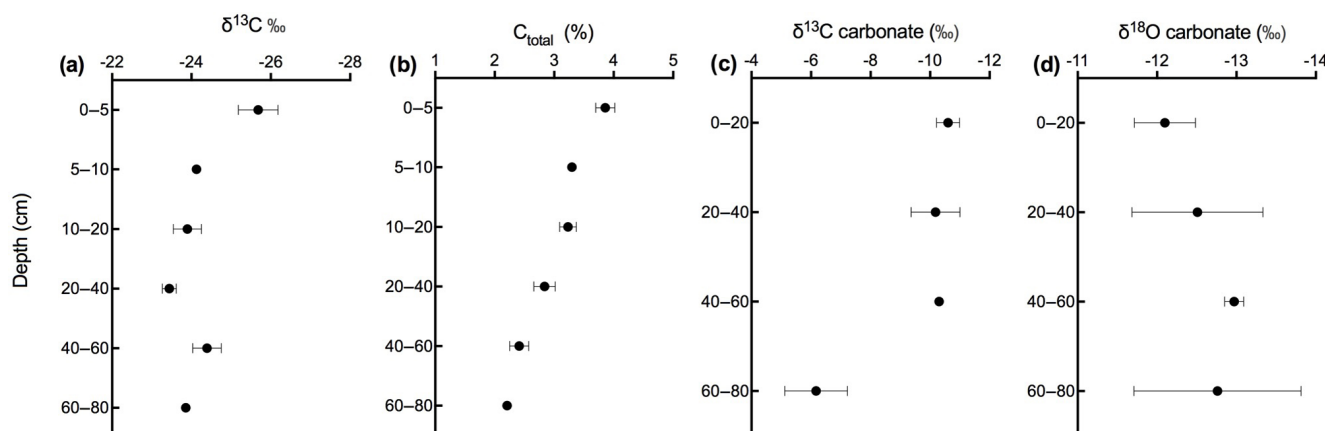


Figure 8. Depth profile of (a) $\delta^{13}\text{C}$, (b) carbon content, (c) $\delta^{13}\text{C}$ of soil carbonate, and (d) $\delta^{18}\text{O}$ of soil carbonate in calcareous soil.

Fig. 8). We observed an increase in $\delta^{13}\text{C}$ values for bulk soil in deeper soil layers (see Fig. 8a, c). Moreover, the carbonate $\delta^{13}\text{C}$ values also got more positive in the 60–80 cm layer. Since total organic carbon content decreases with depth, it can be assumed that the CO₂ derived from carbonate weathering, having less negative $\delta^{13}\text{C}$ values, more strongly contributed to the soil CO₂ (especially since we see an increase in soil CO₂ concentration with depth). This is accordance with the laser-based measurements which showed a strong increase in the $\delta^{13}\text{C}$ of soil CO₂ in the deepest soil layer, leading us to the hypothesis that this signal indicates a strong contribution of carbonate-derived CO₂. Water content, soil CO₂ concentration, and the presence of organic acids or any other source of H⁺ are the major factors influencing carbonate weathering, and variations in soil CO₂ partial pressure, moisture, temperature, and pH can cause degassing of CO₂ which contributes to the soil CO₂ efflux (Schindlbacher et al., 2015; Zamanian et al., 2016). CaCO₃ solubility in pure H₂O at 25 °C is 0.013 g L⁻¹, but in weak acids like carbonic acid, the solubility is increased up to 5 fold (Zamanian et al., 2016). The production of carbonic acid due to CO₂ dissolution will convert carbonate to bicarbonates, resulting in exchange of carbon atoms between carbonates and dissolved CO₂. We assume that at our study site, the topsoil is decar-

bonated due to intensive agriculture for a longer period, thus the soil CO₂ there originates primarily from autotrophic and heterotrophic respiratory activity. In contrast to the deeper soil layers, where the carbonate content is high, CO₂ from carbonate weathering is assumed to be a dominating source of soil CO₂. Also, outgassing of CO₂ from the large groundwater body underneath the calcareous Gleysol might contribute to the inorganic CO₂ sources in the deeper soil, as we found the groundwater table to be 1–2 m below the soil surface. Relative ¹³C enrichment of the CO₂ in the topsoil (4 cm) compared to that at 8 cm depth is probably due to the invasive diffusion of atmospheric CO₂, which has a $\delta^{13}\text{C}$ value close to -8 ‰ (e.g. Levin et al., 1995). The $\delta^{18}\text{O}$ patterns for CO₂ between 4 and 35 cm might reflect the $\delta^{18}\text{O}$ of soil water with stronger evaporative enrichment at the top and ¹⁸O depletion towards deeper soil layers. In comparison, the strong ¹⁸O enrichment of soil CO₂ towards 80 cm in the calcareous Gleysol very likely reflects the ¹⁸O values of groundwater lending further support to the high contribution of CO₂ originating from the outgassing of groundwater. We, however, need then to assume that the oxygen in the CO₂ is not in full equilibrium with the precipitation-influenced soil water. Since mainly microbial carbonic anhydrase mediates the fast equilibrium between CO₂, and water in the soil and

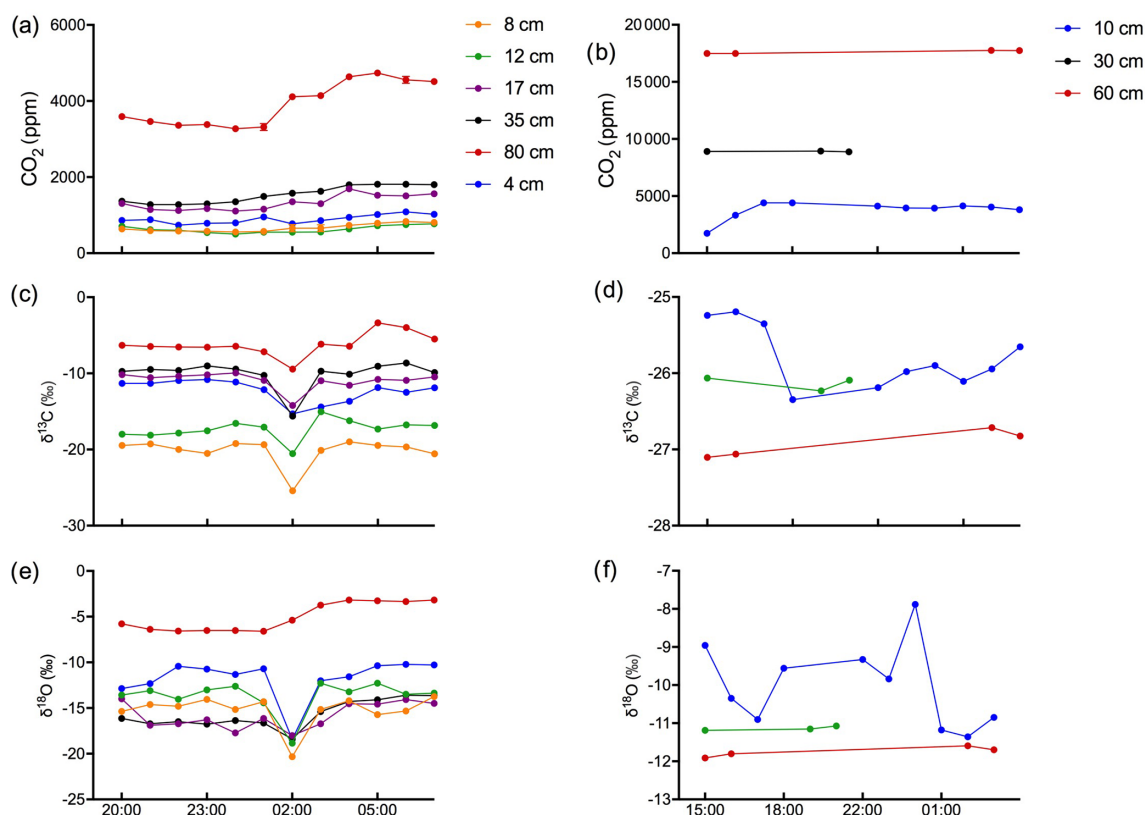


Figure 9. Time course of the evolution of soil gas CO₂ (ppm), $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ in calcareous (a, c, e) and acidic (b, d, f) soils. Data collected continuously over a 12 h time frame for the calcareous soil and a 14 h time window with intermittent data collection for the acidic soil.

the microbial activity is low in deeper soil layers (Schmidt et al., 2011), we speculate that in deep layers with a significant contribution of groundwater derived CO₂ to the CO₂ pool, a lack of full equilibration with soil water might be the reason for the observed $\delta^{18}\text{O}$ values.

Soil CO₂ concentration in the acidic soil showed a positive relationship with soil depth as CO₂ concentration increased along with increasing soil depth (Figs. 9 and 10). CO₂ concentrations were distinctly higher than in the calcareous soil, very likely due to the finer texture than in the gravel-rich calcareous soil. $\delta^{13}\text{C}$ values amounted to approximately -26‰ in 30 and 60 cm depth, indicating the biotic origin from (autotrophic and heterotrophic) soil respiration (Schönwitz et al., 1986). In the topsoil, $\delta^{13}\text{C}$ values did not strongly increase, pointing towards a less pronounced inward diffusion of CO₂ in the acidic soil site, most likely due to more extensive outward diffusion of soil CO₂, as indicated by the still very high CO₂ concentration at 10 cm creating a sharp gradient between soil and atmosphere. Moreover, the acidic soil was rather dense and contained no stones, strongly suggesting that gas diffusivity was rather small. $\delta^{18}\text{O}$ depth patterns of soil CO₂ in the acidic soil most likely reflected $\delta^{18}\text{O}$ values of soil water as CO₂ became increasingly ^{18}O depleted from top to bottom. The $\delta^{18}\text{O}$ of deeper soil layers CO₂ (30–60 cm) was close to the values expected when

full oxygen exchange between soil water and CO₂ occurred (Kato et al., 2004). Assuming an ^{18}O fractionation of 41‰ between CO₂ and water (Brenninkmeijer et al., 1983), this would result in an expected value for CO₂ of $\approx -10 \pm 2\text{‰}$ vs. VPDB CO₂. Corresponding results have been shown for $\delta^{18}\text{O}$ of soil CO₂ using similar hydrophobic gas-permeable membrane tubes used when measuring $\delta^{18}\text{O}$ of soil CO₂ and soil water in situ (Gangi et al., 2015).

4 Conclusions

During our preliminary tests with the OA-ICOS, we found that the equipment was highly sensitive to changes in CO₂ concentrations. We found a non-linear response of the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values against changes in CO₂ concentration. Given the fact that laser-based CO₂ isotope analysers are deployed on site in combination with different gas sampling methods like automated chambers systems (Bowling et al., 2015) and hydrophobic gas-permeable membranes (Jochheim et al., 2018) for tracing various ecosystem processes, it is important to address this issue. Therefore, we developed a calibration strategy for correcting errors introduced in $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurements due to the sensitivity of the device against changing CO₂ concentrations. We

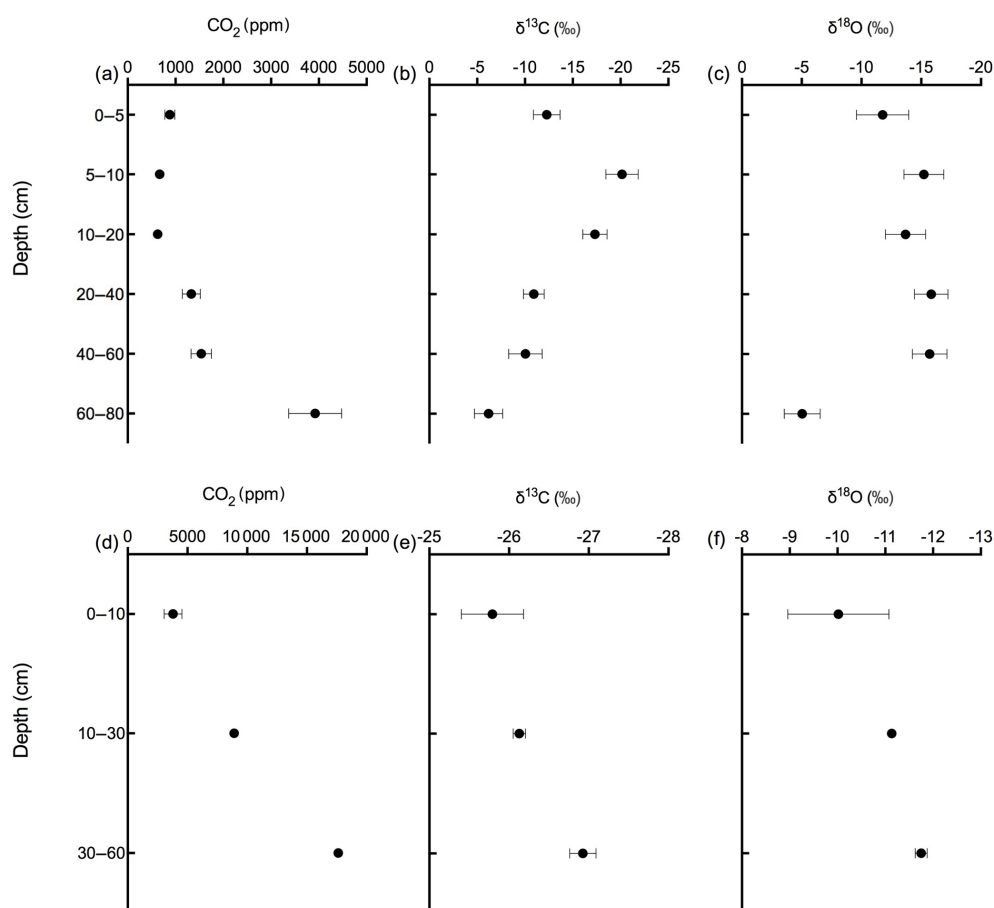


Figure 10. Daily average data of soil CO₂ (ppm), $\delta^{13}\text{C}$, and $\delta^{18}\text{O}$ in calcareous (a, b, c) and acidic (d, e, f) soils across soil depth profiles.

found that the OA-ICOS measures stable isotopes of CO₂ gas samples with a precision comparable to conventional IRMS. The method described in this work for measuring CO₂ concentration and $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values in soil air profiles using an OA-ICOS and hydrophobic gas-permeable tubes is promising and can be applied for soil CO₂ flux studies. As this set-up is capable of measuring continuously for longer time periods at a higher temporal resolution (0.05–0.1 Hz), it offers greater potential to investigate the isotopic identity of CO₂ and the interrelation between soil CO₂ and soil water. By using our measurement set-up, we could identify abiotic as well as biotic contributions to the soil CO₂ in the calcareous soil. We infer that degassing of CO₂ from carbonates due to weathering and evasion of CO₂ from groundwater may leave the soil CO₂ with a specific and distinct $\delta^{13}\text{C}$ signature, especially when the biotic activity is rather low.

Data availability. Data are available via <https://doi.org/10.5281/zenodo.2551237> (Joseph, 2019).

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/soil-5-49-2019-supplement>.

Author contributions. CK, MW, AG, and JJ conceived the idea. JJ conducted the experiments, analyzed the data, and created the figures. JJ, AG, and MW wrote the paper. MS, FH, MA, and CK commented on and edited the paper.

Competing interests. The authors declare that they have no conflict of interest.

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