Calibration of $\delta^{13}C$ and $\delta^{18}O$ measurements in CO_2 using Off axis Integrated Cavity output Spectrometer (OA ICOS)

Jobin Joseph [1], Christoph Kuells [2], Markus Weiler [1]

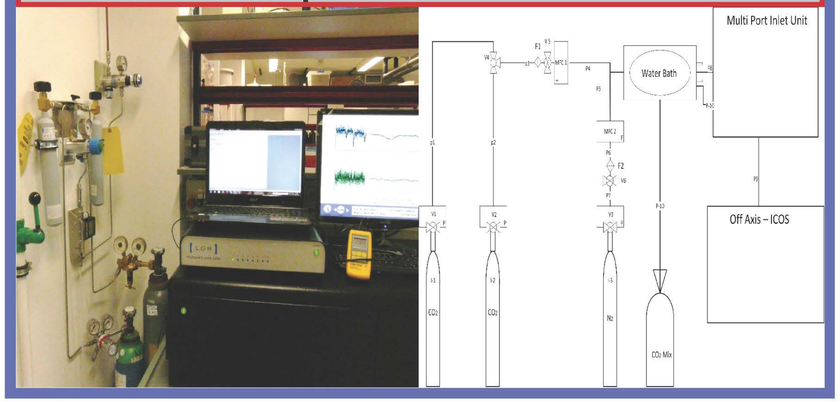
Motivation

The $\delta^{13}C$ and $\delta^{18}O$ of CO_2 have enormous potential as tracers to study and quantify the interaction between the water and carbon cycles. New laser based absorption spectroscopy approaches like Cavity Ring Down Spectroscopy (CRDS) and Integrated Cavity Output Spectroscopy (ICOS) are developed for online measurements of stable isotopes with precision comparable to Isotope Ratio Mass Spectrometry (IRMS). Online sampling and deployment of ICOS require appropriate calibration protocols adapting to the experimental set up.

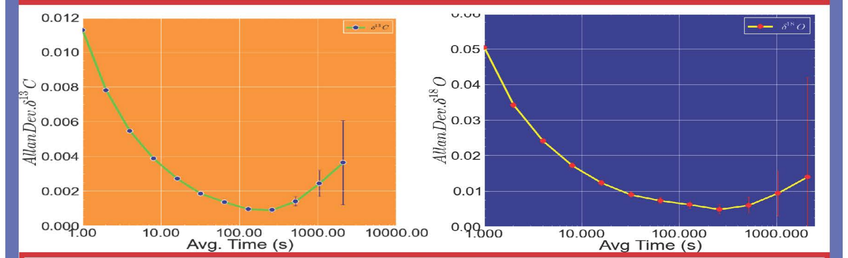
Methodology

The calibration was done for rectifying drifts in $\delta^{13}C$ and $\delta^{18}O$ measurements of an Off Axis ICOS (LGR-CCIA 36-d) due to effects of CO_2 concentration and temperature. CO_2 gases of known $\delta^{13}C$, and $\delta^{18}O$ values; after dilution to a set of varying concentrations, and under varying temperatures were introduced into the device.The drift in the measured data from the real isotopic values were mathematically modelled and corrected by introducing correction factors. The precision assessment for the device was done by creating Allan deviation curves.

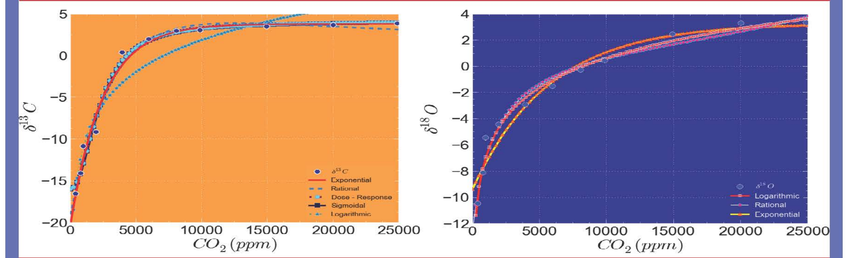
Calibration setup



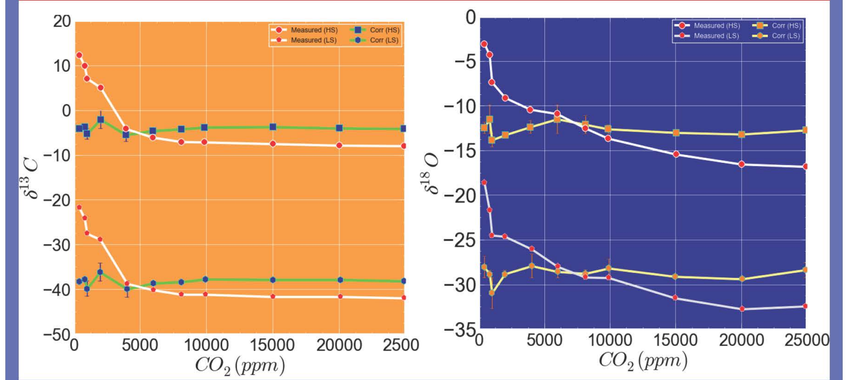
Precision Analysis



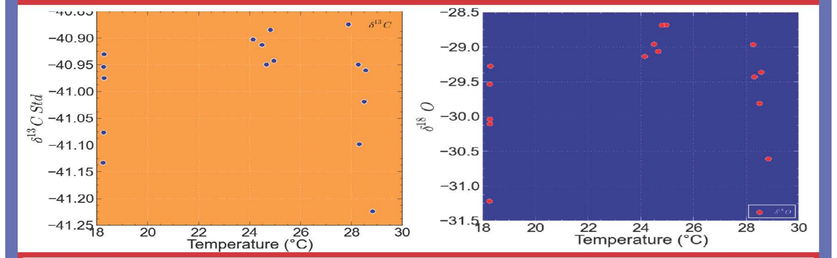
Correction Factor Modelling



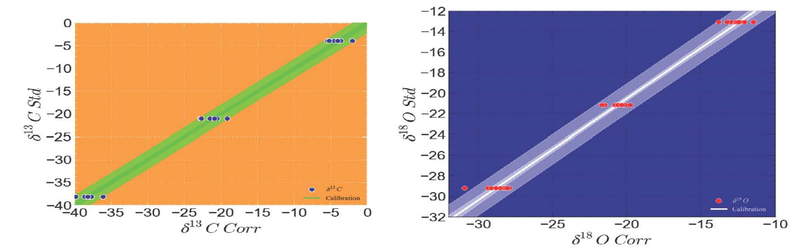
Corrected Isotopic Data



Temperature Effect



Calibration Line



Conclusion

We Introduced a calibration protocol for an Off Axis ICOS (LGR CCIA 36-d) by which stable isotopic data of CO_2 can be measured under varying concentration of CO_2 from 400 ppm to 25,000 ppm. Our findings show, this Off-Axis ICOS is able to measure CO_2 gas samples with an overall accuracy of ~ ±0.98 ‰ for $\delta^{13}C$, ~ ±0.71‰ for $\delta^{18}O$, and an overall precision of ~ ±0.001 ‰ for $\delta^{13}C$, ~ ±0.005‰ for $\delta^{18}O$. This calibration protocol enables online measurement of processes like soil respiration, root respiration, and water infiltration in soil.

enable WCM
KIT Karlsruhe Institute of Technology
Bundesministerium für Bildung und Forschung

(1) Chair of Hydrology, Albert-Ludwigs-University of Freiburg
jobin.joseph@hydrology.uni-freiburg.de www.hydro.uni-freiburg.de

(1) Chair of Hydrology, Albert-Ludwigs-University of Freiburg
markus.weiler@hydrology.uni-freiburg.de www.hydro.uni-freiburg.de

(2) Chair of Hydrology, Albert-Ludwigs-University of Freiburg
christoph.kuells@hydrology.uni-freiburg.de www.hydro.uni-freiburg.de