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Calibration of δ13C and δ18O measurements in CO_2 using Off-axis Integrated Cavity Output Spectrometer (ICOS)

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The δ13C and δ18O of CO_2 has enormous potential as tracers to study and quantify the interaction between the water and carbon cycles. Isotope ratio mass spectrometry (IRMS) being the conventional method for stable isotopic measurements, has many limitations making it impossible for deploying them in remote areas for online or in-situ sampling. New laser based absorption spectroscopy approaches like Cavity Ring Down Spectroscopy (CRDS) and Integrated Cavity Output Spectroscopy (ICOS) have been developed for online measurements of stable isotopes at an expense of considerably less power requirement but with precision comparable to IRMS. In this research project, we introduce a new calibration system for an Off- Axis ICOS (Los Gatos Research CCIA-36d) for a wide range of varying concentrations of CO_2 (800ppm – 25,000ppm), a typical CO_2 flux range at the plant-soil continuum. The calibration compensates for the concentration dependency of δ13C and δ18O measurements, and was performed using various CO_2 standards with known CO_2 concentration and δC13 and δO18 values. A mathematical model was developed after the calibration procedure as a correction factor for the concentration dependency of δ13C and δ18O measurements. Temperature dependency of δ13C and δ18O measurements were investigated and no significant influence was found. Simultaneous calibration of δ13C and δ18O is achieved using this calibration system with an overall accuracy of ($\sim 0.75 \pm 0.24$ ‰ for δ13C, $\sim 0.81 \pm 0.26$‰ for δ18O). This calibration procedure is found to be appropriate for making Off-Axis ICOS suitable for measuring CO_2 concentration and δ13C and δ18O measurements at atmosphere-plant-soil continuum.