



Four years of laser based $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ - CO_2 monitoring in the free troposphere - results, improvements and lessons learned

Lukas Emmenegger, Béla Tuzson, Patrick Sturm, and Stephan Henne

Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for Air Pollution / Environmental Technology, Dübendorf, Switzerland (lukas.emmenegger@empa.ch)

Isotope ratios of trace gases contain highly valuable information about their sources, sinks and transport from the local to the global scale. While isotope ratio mass spectrometry (IRMS) was the method of choice for many years, laser spectroscopy is rapidly gaining importance, because it can deliver real-time, high-precision data at moderate cost and size. Recently, a number of state-of-the-art instruments based on laser absorption spectroscopy appeared on the market, but very few studies have addressed their application in the field.

We have developed and validated an entirely cryogen-free quantum cascade laser absorption spectrometer (QCLAS) using the 4.3 μm spectral range. The instrument is based on the differential absorption technique and suited for long-term, unattended field applications, delivering both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ of CO_2 since December 2008 at the High Altitude Research Station Jungfrauoch (3580 m a.s.l.), Switzerland [1].

The high temporal resolution of the $\delta^{13}\text{C}$ time series allows the detection of pollution events and the application of the Keeling plot method for source signature identification. Backward Lagrangian particle dispersion simulations are used to determine the spatial origin of these CO_2 emission sources. Furthermore, the long data series permits the analysis of yearly, seasonal and daily patterns. Footprint clustering shows significantly different wintertime $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ - CO_2 values depending on the origin and surface residence time of the air masses. In addition, our data reveal that $\delta^{18}\text{O}$, despite its complex nature, is a promising tool to assess the oxygen isotope exchange between atmospheric CO_2 and soil water.

Recent hardware and software upgrades increased the analytical precision to 0.02 ‰ for both $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ - CO_2 at 10 minutes integration time. Furthermore, the calibration strategy was optimized to ensure accuracy and traceability of the long-term data series [2].

We present the current instrumental set-up, the improvements of the most critical parts, and the resulting performance. Then, we discuss methodologies for calibration and data treatment, and illustrate the advantages of measuring high time resolution isotopic signatures of CO_2 in the atmosphere with exemplary results.

[1] Tuzson, B., Henne, S., Brunner, D., Steinbacher, M., Mohn, J., Buchmann, B. and Emmenegger, L. Continuous isotopic composition measurements of tropospheric CO_2 at Jungfrauoch (3580 m a.s.l.), Switzerland: real-time observation of regional pollution events, *Atmospheric Chemistry and Physics*, 2011, 11, 1685–1696.

[2] Sturm, P., Tuzson, B., Henne S., Emmenegger, L. Tracking isotopic signatures of CO_2 at Jungfrauoch with laser spectroscopy: analytical improvements and exemplary results, *Atmospheric Measurement Techniques Discussions*, submitted 2012.