Name of research institute or organization:

Empa – Materials Science and Technology

Title of project:

Continuous measurement of stable CO_2 isotopes at Jungfraujoch, Switzerland

Project leader and team:

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Project description:

The analysis of the isotopic composition of atmospheric CO_2 is a major tool to study the source- and sink strengths, as well as the fate of anthropogenically emitted CO_2 at local, regional and global scales. Discrete samples, analyzed by isotope ratio mass spectroscopy, have been used in atmospheric research for many years. Even more insight into a wide range of processes and their dynamics can be obtained by real-time measurements with high temporal resolution. For this purpose, we developed a quantum cascade laser based absorption spectrometer (QCLAS) to perform in-situ and high precision isotope ratio measurements of CO_2 in the free troposphere at Jungfraujoch. The three main CO_2 isotopologue mixing ratios ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$) have simultaneously been monitored since December 2008, providing the first long-term, continuous time series at a remote location.

In 2012, mainly two goals were accomplished. First, significant updates on the instrument and the calibration procedures were implemented to further improve the data quality (Figure 1). A precision of 0.02 ‰ for both isotope ratios ($\delta^{13}C$ and $\delta^{18}O$) is now obtained for an averaging time of 10 minutes. The long-term accuracy is assured through a set of secondary and working standards calibrated against VPDB by IRMS.

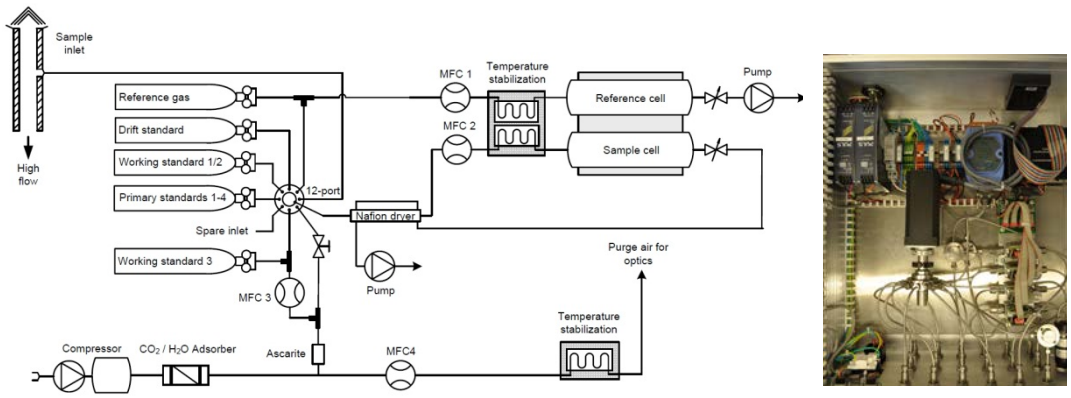

Figure 1. Schematic of the gas sampling setup and photograph of the newly developed gas handling and calibration module.

Second, the whole time series of the four year period was processed (Figure 2). Its analysis reveals mean annual cycles between December 2008 and September 2012 with peak-to-peak amplitudes of 11 µmol·mol^{-1} for CO_2, 0.60 ‰ for $\delta^{13}C$ and 0.81 ‰ for $\delta^{18}O$. The high temporal resolution of the measurements also allows capturing variations on hourly and diurnal time scales. For CO_2, the mean diurnal peak-to-peak amplitude is about 1 µmol·mol^{-1} in spring, autumn and winter, and about twice as high in summer. The mean diurnal

variability in the isotope ratios is largest during the summer months too, with an amplitude of 0.1 ‰ for both $\delta^{13}C$ and $\delta^{18}O$, and a smaller or not discernible diurnal cycle during the other seasons. The day-to-day variability, however, is much larger and depends on the origin of the air masses arriving at Jungfraujoch.

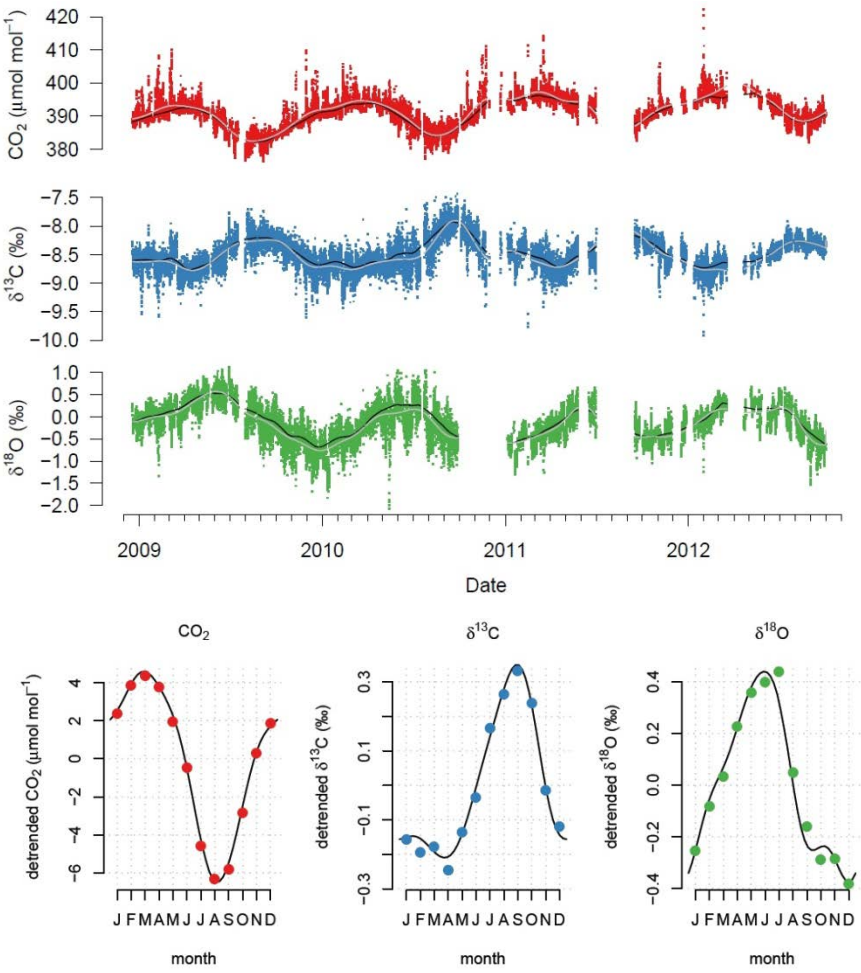

Figure 2. Overview of the data records from December 2008 to September 2012 (top). Hourly averaged data of CO_2*, and isotopic ratios* $\delta^{13}C$ *and* $\delta^{18}O$ *as well as fitted background curves (black: local regression, grey: smooth curve fit) are shown. Mean seasonal cycles from detrended and monthly bin-averaged data and the annual harmonic part of the smoothed curve fit (bottom).*

A major benefit of the high-time resolution measurements compared to the traditional flask sampling is that, in addition to seasonal variations and long-term trends, also variations on hourly and diurnal time scales can be captured. This allows for combining the measurements with meteorology and to interpret the data in terms of atmospheric dynamics. Using backward Lagrangian particle dispersion model simulations, a close link between air composition and prevailing transport regimes has been established, which explains much of the observed variability in terms of transport history and influence region. A footprint clustering shows significantly different wintertime CO_2, $\delta^{13}C$ and $\delta^{18}O$ values, depending on the origin and surface residence times of the air masses.

Key words:

Isotope ratio measurements, carbon dioxide, laser spectroscopy, quantum cascade laser

Collaborating partners/networks:

Max-Planck-Institute for Biogeochemistry, Jena, Germany
ETHZ - Inst. for Quantum Electronics, Switzerland
Alpes Lasers SA, Switzerland
University of Bern, Switzerland

Scientific publications and public outreach 2012:

Refereed journal articles and their internet access

Sturm, P., B. Tuzson, S. Henne, and L. Emmenegger, Tracking isotopic signatures of CO_2 at Jungfraujoch with laser spectroscopy: analytical improvements and exemplary results, accepted for Atmos. Meas. Tech. Discuss, 2012.

Conference papers

Emmenegger, L., J. Mohn, P. Sturm, S. Henne, P. Wunderlin, J. R. Köster, S. Eyer and B. Tuzson, Application of direct absorption mid IR laser spectroscopy for isotope specific detection of greenhouse gases, 15th International Conference on Laser Optics, St. Petersburg, Russia, June 25-29, 2012.

Sturm, P., B. Tuzson, S. Henne, and L. Emmenegger, Tracking isotopic signatures of CO_2 at Jungfraujoch with high-precision laser spectroscopy: analytical improvements, calibration and exemplary results, Joint European Stable Isotope Users group Meeting (JESIUM 2012), Leipzig, Germany, September 02-07, 2012.

Sturm, P., B. Tuzson, S. Henne, and L. Emmenegger, Tracking isotopic signatures of CO_2 at Jungfraujoch with high-precision laser spectroscopy, Fall Meeting of the Swiss Chemical Society, Zürich, Switzerland, September 13, 2012.

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