Name of research institute or organization:

Empa – Materials Science and Technology

Title of project:

Continuous measurement of stable CO_2 isotopes at Jungfraujoch, Switzerland

Part of this programme:

ICOS

Project leader and team:

Lukas Emmenegger, project leader
Béla Tuzson
Stephan Henne
Lea Jacot

Project description:

It is the 5th year of continuous and *in-situ* isotopic composition measurement of atmospheric CO_2 performed at high temporal resolution (1s) deploying a mid-infrared quantum cascade laser based absorption spectrometer. The data represents the longest time-series of this kind. The three main CO_2 isotopologue mixing ratios ($^{12}C^{16}O_2$, $^{13}C^{16}O_2$ and $^{12}C^{18}O^{16}O$) are simultaneously monitored at a precision of < 0.03‰, routinely obtained after 10 min averaging (Figure 1).

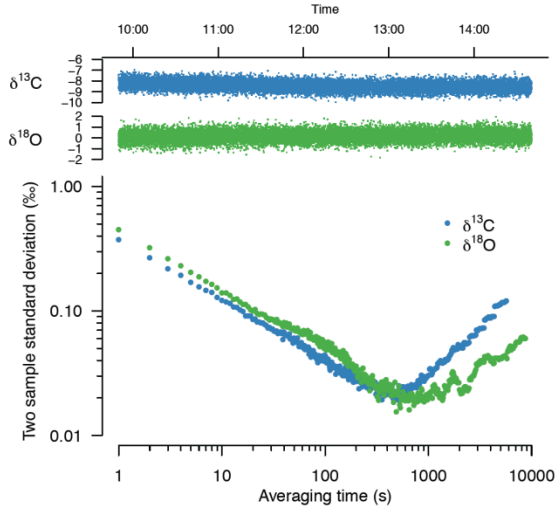

Figure 1. Two-sample standard deviation (Allan deviation) plot of pressurized air measurements for $\delta^{13}C$ and $\delta^{18}O$ of CO_2. The optimum averaging time is reached after 12 min for both isotope ratios, corresponding to an analytical precision of 0.02 ‰. This long-term instrumental stability is a result of the better temperature, pressure and laser frequency control. As a consequence, the interval for the drift standard measurements was increased by a factor two leading to reduced reference gas consumption.

The long-term accuracy and data quality is assured by maintaining a set of working standards which are systematically compared to primary standards, calibrated against VPDB by IRMS, stored at the station (Table 1).

Table 1. Primary standards with the assigned values on the WMOX2007scale for CO_2 and the VPDB-CO_2 scale for $\delta^{13}C$ and $\delta^{18}O$.

Tank ID	Mixture	CO_2 (ppm)	$\delta^{13}C$ (‰)	$\delta^{18}C$ (‰)
CB08984	CO_2 + syn. air	383.40	−3.54	−14.11
CB08970	CO_2 + syn. air	394.43	−8.00	−17.38
CB08999	CO_2 + syn. air	388.36	−12.01	−20.52
3076	compressed air	429.06	−10.57	−7.65

The hardware updates accomplished in 2012 with the aim of optimizing long-term operation, i.e. temperature stability, automatized calibration process and reference gas consumption, allowed us to develop a complete software package for fast data retrieval and analysis. A dedicated graphical user interface has been implemented using Igor Pro (Wavemetrics, Inc., USA.) to aid data handling and visualization. Using this analytical tool, the whole time series was processed (see Figure 2).

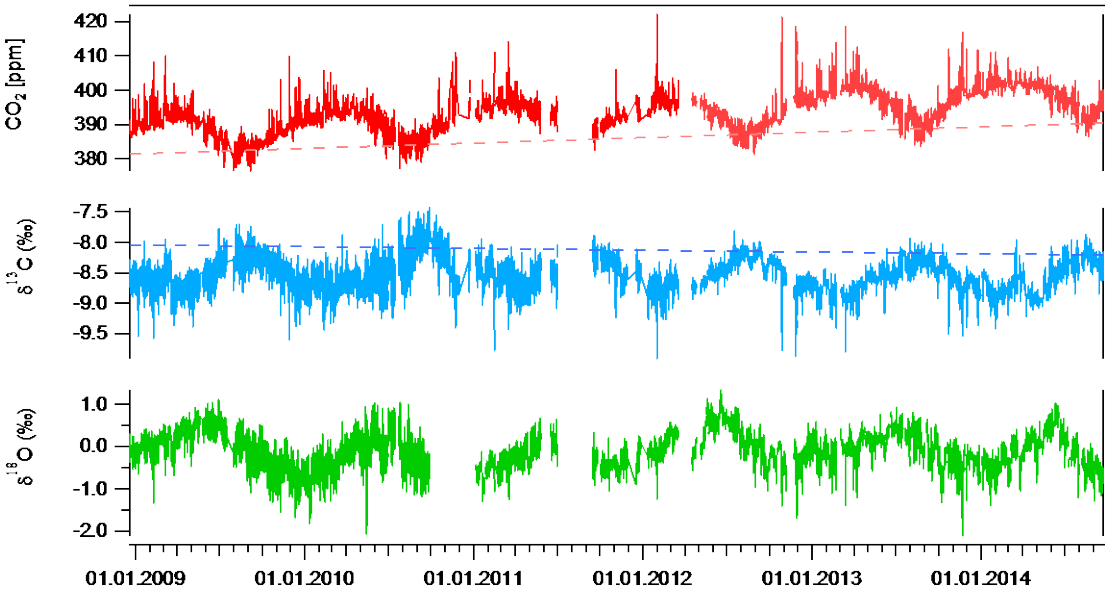

Figure 2. Overview of the data record from January 2009 to September 2014. The plotted CO_2 and isotopic ratios $\delta^{13}C$ and $\delta^{18}O$ are hourly averaged data. A long-term trend observed in the time-series is qualitatively indicated by a linear fit through the minima of the yearly cycles (dashed lines).

The results indicate that since the instrument hardware/software update in March 2012 the measurements are uninterrupted and show less scatter in the isotope ratio values compared to the previous period. Therefore, our ability to confine emission source signatures has significantly improved, and we expect to obtain more robust statistics on the various CO_2 emission sources using Lagrangian transport model simulations and footprint clustering. As the CO_2 isotope measurements are continuing and because of the increased data quality, we expect to be able to analyze distinct events and tracer relationships depending on weather conditions and attribute these to specific emission/uptake regions and processes.

Key words:
Isotope ratio measurements, carbon dioxide, laser spectroscopy, quantum cascade laser

Collaborating partners/networks:
Max-Planck-Institute for Biogeochemistry, Jena, Germany
University of Berne, Switzerland
ETH Zürich - Inst. for Quantum Electronics, Switzerland
Alpes Lasers SA, Switzerland

Scientific publications and public outreach 2014:

Conference papers

Emmenegger, L., High-precision MIR trace gas analysis for environmental applications, MIRIFISENS Workshop, Zürich, Switzerland, January 14-15, 2014.

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Address:

Empa
Laboratory for Air Pollution and Environmental Technology
Überlandstrasse 129
CH-8600 Dübendorf

Contacts:

Dr. Lukas Emmenegger
Tel.: +41 58 765 4699
Fax: +41 58 765 6244
e-mail: lukas.emmenegger@empa.ch
URL: http://empa.ch/abt134