

Name of research institute or organization:

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**Empa, Swiss Federal Laboratories for Materials Science and Research**

Title of project:

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Continuous measurement of stable CO<sub>2</sub> isotopes at Jungfraujoeh, Switzerland

Project leader and team:

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Project description:

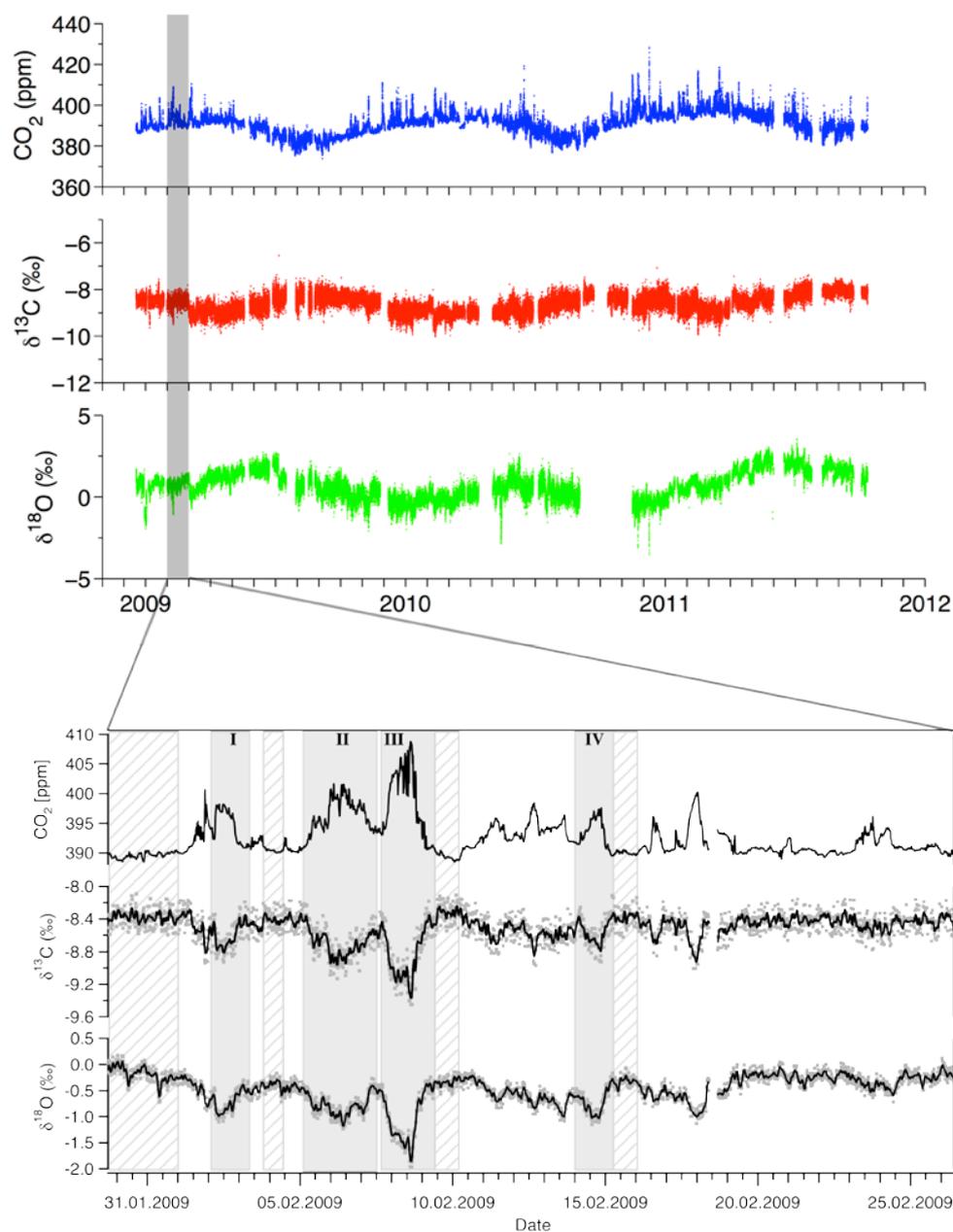
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Isotope ratios of CO<sub>2</sub> are highly valuable to investigate CO<sub>2</sub> sources, sinks and fate at local, regional and global scales. This is possible because the physical and biochemical processes that are involved in the carbon cycle lead to characteristic isotopic fractionation.

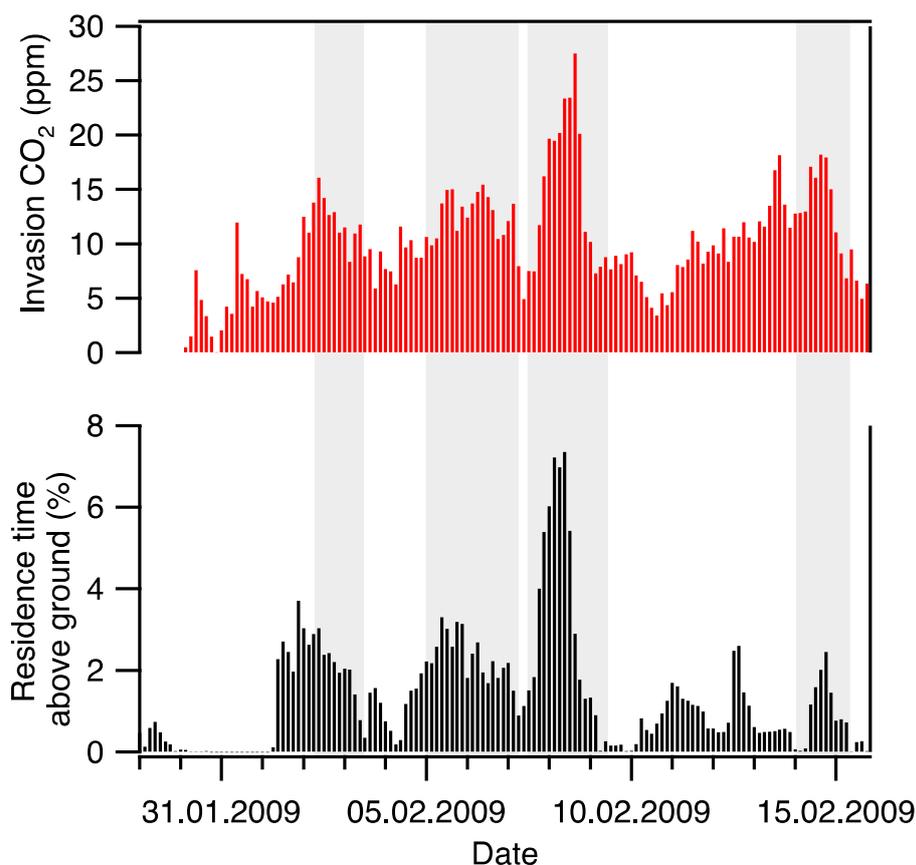
A quantum cascade laser absorption spectrometer (QCLAS) is used to perform in-situ, continuous and high precision isotope ratio measurements of CO<sub>2</sub> in the free troposphere at Jungfraujoeh. The three main CO<sub>2</sub> isotopologue mixing ratios (<sup>12</sup>C<sup>16</sup>O<sub>2</sub>, <sup>13</sup>C<sup>16</sup>O<sub>2</sub> and <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O) are simultaneously detected with one-second time resolution since December 2008 at Jungfraujoeh (Figure 1), providing the first long-term, continuous time series for a remote location. The one-second precision is 0.29‰ for both δ<sup>13</sup>C and δ<sup>18</sup>O. Allan variance analysis shows a minimum at 50s corresponding to a precision of 0.046‰ for both isotope ratios.

Detailed data analysis was performed for a winter period in February 2009 (Figure 1). During this period, various pollution events from anthropogenic emissions were identified based on changes in the relation between CO<sub>2</sub> and carbon monoxide (CO) mixing ratios. Each of these events shows significant changes in δ<sup>13</sup>C and δ<sup>18</sup>O, which can be used to determine CO<sub>2</sub> source signatures using the Keeling intercept method. Furthermore, these signatures can also be linked to source regions using a backward Lagrangian particle dispersion model (LPDM). This showed that the polluted air masses mainly originated from northern Italy, eastern France, Benelux region and southern Germany.

In addition, the data revealed that the δ<sup>18</sup>O values are strongly influenced by the invasion process (CO<sub>2</sub> isotopically equilibrating with soil water). Using a simple isotopic mass balance for δ<sup>18</sup>O, the amount of atmospheric CO<sub>2</sub> that exchanged its oxygen isotope with soil water was estimated. Independent calculations from the particle dispersion model show that the pattern of CO<sub>2</sub> interacting with soil is strikingly similar to the residence time of the air masses above ground (Figure 2).



**Figure 1.** Time series of tropospheric  $\text{CO}_2$  mixing ratio and its isotopic composition from December 2008 until October 2011 (top) and enlarged for February 2009 (bottom). The dots represent 10 min averages, while the solid line is an interpolation using a smoothing spline. The shaded areas indicate four distinct pollution events (I-IV), while hatched areas highlight periods with the free tropospheric background conditions.



**Figure 2.** (top) Amount of atmospheric CO<sub>2</sub> that exchanged its oxygen isotope with soil water. (bottom) Residence time of the air masses in a layer up to 100m above ground relative to the total residence time (5 days) as calculated from the LPDM.

Key words:

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

Collaborating partners/networks:

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

Scientific publications and public outreach 2011:

**Refereed journal articles and their internet access**

Tuzson, B., Henne, S., Brunner, D., Steinbacher, M., Mohn, J., Buchmann, B. and Emmenegger, L., Continuous isotopic composition measurements of tropospheric CO<sub>2</sub> at Jungfraujoch (3580 m a.s.l.), Switzerland: real-time observation of regional pollution events. *Atmos. Chem. Phys.*, 11: 1685–1696, doi:10.5194/acp-11-1685-2011, www.atmos-chem-phys.net/11/1685/2011/, 2011.

### **Conference papers**

Emmenegger, L., Tuzson, B., Mohn, J., Brunner, D., Henne, S., Kammer, A., Zeeman, M.J., Measurements of stable CO<sub>2</sub> isotopic species using mid IR laser spectroscopy – development and environmental applications, ANAKON 2011, Zürich, Switzerland, 2011.

Emmenegger, L., Tuzson, B., Mohn, J., Recent developments in real-time measurements of CO<sub>2</sub> and N<sub>2</sub>O stable isotopes based on QC laser spectroscopy, Annual Meeting of the German Association for Stable Isotope Research - GASIR 2011, Villigen, Switzerland.

Emmenegger, L., Wunderlin, P., Köster, J.R., Manninen, A., Mohn, J., CO<sub>2</sub> and N<sub>2</sub>O isotopic ratio measurements by QCL spectroscopy – recent developments and environmental applications, 8th International Conference on Tunable Diode Laser Spectroscopy TDLS, Zermatt, Switzerland, 2011.

Tuzson, B., Mohn, J., Steinbacher, M., Henne, S., Brunner, D., Buchmann, B. and Emmenegger, L., Continuous and in situ isotopic composition measurements of tropospheric CO<sub>2</sub> at Jungfrauoch: real-time observation of regional pollution events. Isotopes 2011, Gréoux-les-Bains, France, 2011.

Sturm, P., Tuzson, B., Henne, S., Brunner, D., Steinbacher, M., Mohn, J., Buchmann, B. and Emmenegger, L., Continuous isotopic composition measurements of tropospheric CO<sub>2</sub> at Jungfrauoch, Switzerland, GEO-Carbon Conference, Rome, Italy, 2011.

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