

Name of research institute or organization:

**Max Planck Institut für Biogeochemie, Jena**

Title of project:

Flask comparison on Jungfrauoch

Project leader and team:

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Project description:

The European project IMECC (Infrastructure for Measurements of the European Carbon Cycle) that finished some time ago had an activity called Transnational Access (TA). It was designed to enable high-precision measurements for European research institutions and, thus, to broaden and improve access to European Carbon Cycle measurement facilities. One of these facilities is the Research Station at Jungfrauoch.

MPI-BGC Jena had submitted a proposal to get access to this research station which was approved in 2008. The goal behind this TA activity is to compare CO<sub>2</sub> and O<sub>2</sub> concentrations of air samples taken simultaneously at Jungfrauoch station via combined flask filling. The Jena MPI has supplied the research station at Jungfrauoch with a flask sampling unit of the typical MPI-BGC design. This is run in conjunction with the Groningen (project Bert Kers, Groningen) as well as UBern (project Markus Leuenberger, Bern) flask sampling programmes.

The main outcome of the collaborative flask sampling was summarized by Ingrid van der Laan-Luijkx et al., published in AMTD [2012]. The three laboratories report the following average standard errors in the mean of the duplicate or triplicate for CO<sub>2</sub>, δO<sub>2</sub>/N<sub>2</sub> and δ<sup>13</sup>CO<sub>2</sub>. These numbers are of similar quality for UBE and RUG and better for MPI. Regarding δ<sup>13</sup>CO<sub>2</sub> this has to do with the different techniques and very different sample amounts that are used for the analyses. For UBE, only 0.5 ml STP of air is used for the carbon isotope determination whereas for the other two laboratories amounts of up to 600 ml are used.

	UBE	RUG	MPI
CO <sub>2</sub> (ppm)	0.05	0.06	0.06
δ (O <sub>2</sub> /N <sub>2</sub> ) (per meg)	6	8	3
δ <sup>13</sup> CO <sub>2</sub> (‰)	0.08	0.07	0.009

Table 1: Average standard errors in the mean of the duplicate or triplicate flasks for the CO<sub>2</sub>, δ(O<sub>2</sub>/N<sub>2</sub>) and δ<sup>13</sup>CO<sub>2</sub> measurements from each of the three laboratories.

It is obvious from Table 2, that the agreement for the CO<sub>2</sub> concentration is fairly good with a mean offset between the laboratories of around 0.2 ppm, Bern values being higher. Even high values (regional or local contamination) deviating significantly from the background values are in rather good agreement. The largest deviations are about 2 ppm in absolute (not shown). However, the offsets are significantly larger for oxygen between the three laboratories. For δ<sup>13</sup>CO<sub>2</sub> it looks rather good regarding the offsets but the noise of the data among the three institutes is large as shown in Figure 2. Most probably the different measuring technique with the extremely low amount used at UBE is not fully adequate for such high precision measurements, it was originally developed for ice core measurements for which the focus was on very small sample amounts in order to minimize the ice sample size.

	UBE – RUG		UBE – MPI		MPI – RUG	
	average	stdev	average	stdev	average	stdev
CO <sub>2</sub> (ppm)	0.20 ± 0.06	0.6	0.08 ± 0.05	0.4	0.14 ± 0.06	0.5
CO <sub>2</sub> (part 1)	0.18 ± 0.06	0.3	0.21 ± 0.05	0.3	0.042 ± 0.07	0.3
CO <sub>2</sub> (part 2)	0.21 ± 0.09	0.7	0.01 ± 0.07	0.5	0.19 ± 0.08	0.6
δ (O <sub>2</sub> /N <sub>2</sub> ) (per meg)	-33 ± 4	40	-31 ± 4	30	-3 ± 3	26
δ (O <sub>2</sub> /N <sub>2</sub> ) (part 1)	-33 ± 6	30	-14 ± 6	30	-16 ± 4	20
δ (O <sub>2</sub> /N <sub>2</sub> ) (part 2)	-37 ± 5	40	-38 ± 4	30	1 ± 4	27
δ <sup>13</sup> CO <sub>2</sub> (‰)	-0.03 ± 0.04	0.3	-0.02 ± 0.03	0.22	-0.02 ± 0.03	0.20
δ <sup>13</sup> CO <sub>2</sub> (part 1)	-0.06 ± 0.05	0.25	0.00 ± 0.07	0.20	-0.13 ± 0.04	0.10
δ <sup>13</sup> CO <sub>2</sub> (part 2)	-0.02 ± 0.05	0.3	-0.02 ± 0.03	0.23	-0.00 ± 0.03	0.21

Table 2: Average CO<sub>2</sub>, δ(O<sub>2</sub>/N<sub>2</sub>) and δ<sup>13</sup>CO<sub>2</sub> differences between each set of two laboratories and their standard errors in the mean. Also given are the standard deviations. The results are given for the entire data set as well as for the two sub-periods: before March 2009 (part 1) and after March 2009 (part 2).

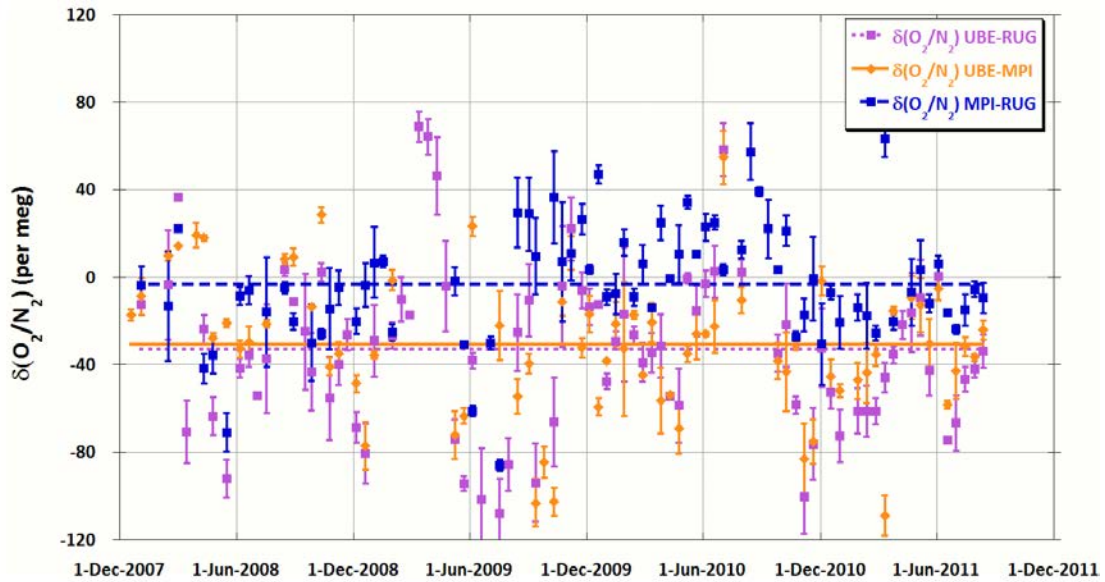


Figure 1: Differences of the δ(O<sub>2</sub>/N<sub>2</sub>) values measured by each set of two laboratories. Also indicated are the average differences. These are: -33 per meg for UBE-RUG, -31 per meg for UBE-MPI and -3 per meg for MPI-RUG. The error bars represent the quadratically added standard errors of the measurements of the two laboratories.

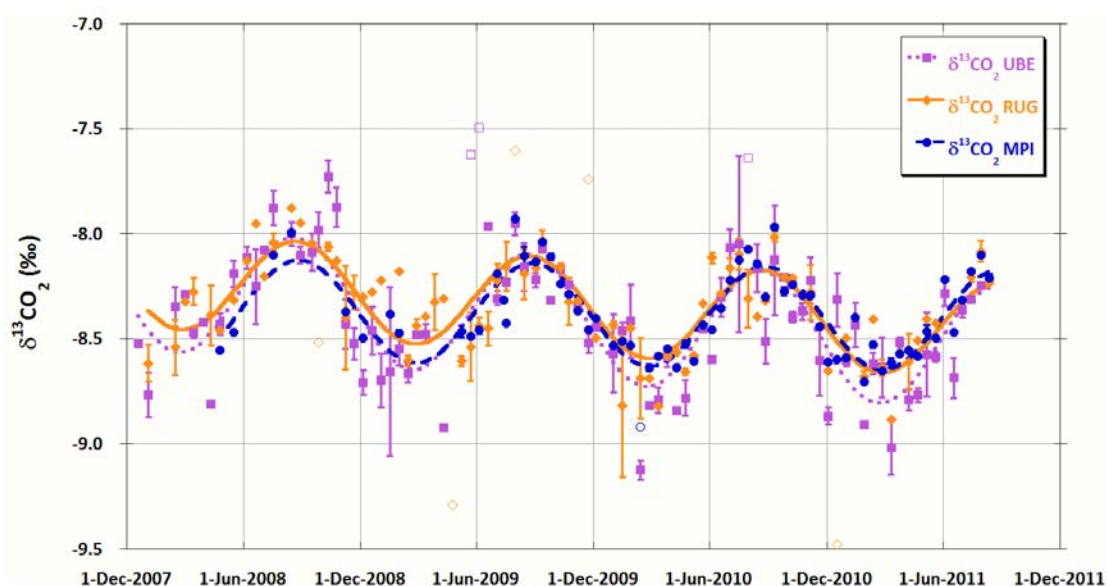


Figure 2:  $\delta^{13}\text{CO}_2$  observations from Jungfraujoch, Switzerland from flask samples measured by three laboratories: UBE (pink squares), RUG (orange diamonds) and MPI (blue circles). The values are the averages of 1, 2 or 3 flasks. The fits through the data are linear trends and single harmonic seasonal components. Open symbols represent those values that are outliers to the fit of the individual data set. The error bars represent the standard error of the average value of 2 or 3 flasks. For single flask measurements error bars are not shown.

The trend analysis revealed significant differences among the three laboratory data sets. The best agreement was obtained for the  $\text{CO}_2$  concentrations for which the average trend lies within the uncertainties of all three labs. Similar results are obtained for the amplitude of  $\text{CO}_2$ . The view is very different for oxygen. A too large negative trend was observed by UBE data set. Since this data set shows the highest variability it is worthwhile applying a stronger filtering process. If this is done as noted in the footnote a) of table 3, a more realistic number of  $-21 \pm 2$  per meg per year is obtained. This value compares much better with the RUG and MPI values of  $-23 \pm 3$  and  $-17.3 \pm 1.5$  per meg per year. The amplitude remains lower even after this stronger filtering with  $73 \pm 3$  per meg for UBE compared to  $85 \pm 3$  and  $84.1 \pm 2.2$  per meg for RUG and MPI. Trends for  $\delta^{13}\text{CO}_2$  are very different (Table 3) but strongly influenced by the noise of the corresponding data sets. This is documented by the UBE values when comparing the full data set that gives a trend of  $-0.013 \pm 0.004$  ‰ to the restricted data set of parallel flask measurements yielding  $-0.081 \pm 0.018$  ‰.

	UBE	RUG	MPI
Trend $\text{CO}_2$ ( $\text{ppm yr}^{-1}$ )	$1.76 \pm 0.17$	$1.94 \pm 0.18$	$1.83 \pm 0.17$
Amplitude $\text{CO}_2$ (ppm)	$10.3 \pm 0.3$	$10.6 \pm 0.4$	$10.7 \pm 0.3$
Trend $\delta(\text{O}_2/\text{N}_2)$ (per meg $\text{yr}^{-1}$ )	$-29^a \pm 3$	$-23 \pm 3$	$-17.3 \pm 1.5$
Amplitude $\delta(\text{O}_2/\text{N}_2)$ (per meg)	$69^a \pm 5$	$85 \pm 4$	$84.1 \pm 2.2$
Trend $\delta^{13}\text{CO}_2$ ( $\text{‰ yr}^{-1}$ )	$-0.081^b \pm 0.018$	$-0.069 \pm 0.015$	$-0.016 \pm 0.014$
Amplitude $\delta^{13}\text{CO}_2$ (‰)	$0.592 \pm 0.028$	$0.455 \pm 0.022$	$0.485 \pm 0.018$

<sup>a</sup> More realistic values are obtained when a stronger filter is applied to the data:  $-21 \pm 2$  per meg  $\text{yr}^{-1}$  and  $73 \pm 3$  per meg for the linear trend and seasonal amplitude respectively. <sup>b</sup> The trend estimate based on the complete record available for UBE between 2000 and 2012 is:  $-0.013 \pm 0.004$  ‰.

Table 3:  $\text{CO}_2$ ,  $\delta(\text{O}_2/\text{N}_2)$  and  $\delta^{13}\text{CO}_2$  trends and seasonal amplitudes based on the fit of the data sets from each laboratory: UBE, RUG and MPI. The used fit is a linear combination of a linear trend and a double (for  $\text{CO}_2$ ) or single (for  $\delta(\text{O}_2/\text{N}_2)$  and  $\delta^{13}\text{CO}_2$ ) harmonic seasonal component.

Key words:

Flask measurements, inter-comparison, oxygen and carbon dioxide measurements, greenhouse gas

Collaborating partners/networks:

IMECC partners

Scientific publications and public outreach 2012:

**Refereed journal articles and their internet access**

van der Laan-Luijkx, I.T., S. van der Laan, C. Uglietti, M.F. Schibig, R.E.M. Neubert, H.A.J. Meijer, W.A. Brand, A. Jordan, J.M. Richter, M. Rothe, and **M.C. Leuenberger**, Atmospheric CO<sub>2</sub>, δ(O<sub>2</sub>/N<sub>2</sub>) and δ<sup>13</sup>CO<sub>2</sub> measurements at Jungfrauoch, Switzerland: results from a flask sampling intercomparison program, Atmos. Meas. Tech. Discuss., 5, 7293-7322, doi:10.5194/amtd-5-7293-2012, 2012.  
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