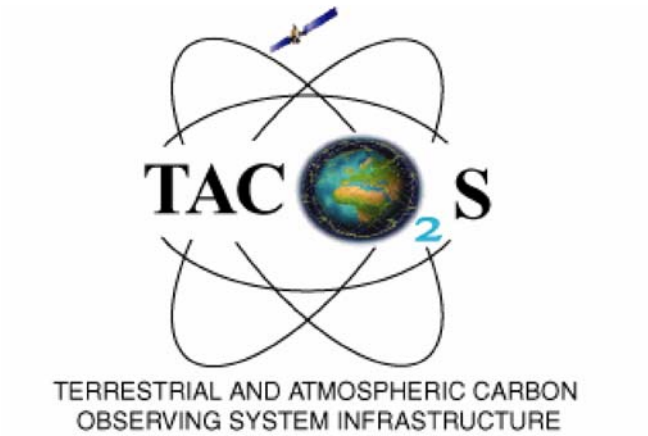
TACOS-Infrastructure



SPECIAL REPORT # 2

Results of inter-comparison programme for analysis of “sausage” flask air samples

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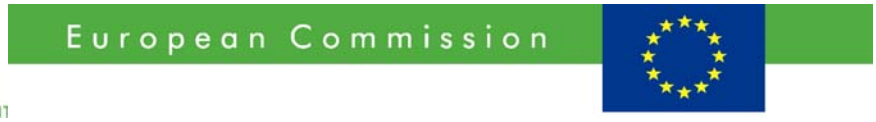

Special Report 2

Results of inter-comparison programme for analysis of “sausage” flask air samples

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Introduction

Starting at the beginning of the project in 2002 with a regular procedure [Levin et al., 2002a], Sausage Flask Intercomparison was continued and extended in 2003 as an ongoing TACOS activity. In October 2002 the National Institute for Environmental Studies (NIES) was included in the intercomparison project as Lab 6. Thus, from sausage 5 onwards at the Heidelberg Institut für Umweltphysik (UHEI-IUP = Lab 1) every two months, three sets of 14 flasks were filled as a sausage with natural air from a pressurised tank and distributed to five laboratories (LSCE = Lab 2, MPI-BGC = Lab 3, CAR = Lab 4, CIO-RUG = Lab 5, NIES = Lab 6). In the recent report, the results for CO_2 and stable isotope ratios as well as for CH_4 from nine intercomparison experiments are presented. The filling procedure is the same as described in the last year's report; for measurement techniques and calibration procedures in the different labs see Levin et al. [2002b] and references therein.

Drift corrections for CO_2 flask results of UHEI-IUP, LSCE, MPI-BGC and CAR

The drift of CO_2 mixing ratios in the standard flasks used in our European projects (AEROCARB and TCOS Siberia) is one of the major sources of uncertainty, also within this intercomparison project. While the first flask pair for UHEI-IUP (the first and the 12^{th} flask in the sausage) is normally measured within one week after filling, analysis in the other labs, in particular when located outside Europe, can be performed only several weeks after filling. Respective drift corrections can then be on the order of 0.1 ppm, as large as the target precision for laboratory intercomparability of CO_2 when data sets shall be merged. Considerable effort has, therefore, been put into storage drift determination in the participating labs, and a consistent correction factor was found at LSCE and at UHEI-IUP, namely 0.0027 ± 0.0013 ppm per day of storage [Frese, 2004]. A very similar value of 0.0025 ± 0.0011 ppm per day was found when comparing the first pair of UHEI-IUP with the second one analysed after 2-3 months as a control (UHEI after). We, therefore, use here the revised storage correction for CO_2 of 0.0027 ppm per day for all sausage flask evaluations of UHEI-IUP, LSCE, MPI-BGC and CAR.

Results

As in our last year's report we present the intercomparison results as deviations of individual labs from the results determined at UHEI-IUP on the first flask pair. The disadvantage is that all lab differences are biased by the scatter of the Heidelberg measurements. On the other hand, this allows us to directly compare all differences between the other laboratories. Only in the case of CH_4, a second Figure (4b) was prepared showing all results as deviations from CAR, as CAR has the longest experience in CH_4 analysis of all groups. However, also in this case the general scatter of the deviations was not reduced.

CO_2 mixing ratios:

Figure 1a shows the differences of flask pair means of individual sausages analysed in individual labs from the mixing ratio determined at UHEI-IUP on the first flask pair (i.e. "UHEI-IUP minus LABx"), plotted against the mixing ratio determined in the filling tank. Most of the deviations are negative which means that UHEI-IUP measures lower values than all other labs by 0.15 to 0.35 ppm (see Table 1). An offset of this magnitude was also found in WMO Round-Robin Intercomparison Experiments [Peterson et al., 2002], and when analysing the most recently calibrated standard gases purchased at NOAA/CMDL (CO_2 Central Calibration Lab). A correction of the UHEI-IUP scale will be applied in the near future, but is not performed at this moment because the magnitude of the correction may change when NOAA reports their revised calibration values to the "Users" - hopefully within the next half year. Figure 1b shows the respective mean differences between UHEI-IUP and LABx of three sausages filled at a time against filling date. This Figure allows us to inspect the stability of

interlaboratory differences over time. Except for CIO, all differences show standard deviations on the order of 0.08 to 0.12 ppm. UHEI-IUP itself shows a standard deviation of 0.09 ppm when comparing mean results of measurements in flask pairs which are 2 to 3 months apart. Most of the uncertainty is obviously due to the precision of measurements in the different labs, and also due to the uncertainty of the storage correction as the pair agreement within the individual labs is very well comparable. All in all the yet achieved intercomparability is very promising, and already close to the WMO target of 0.1 ppm.

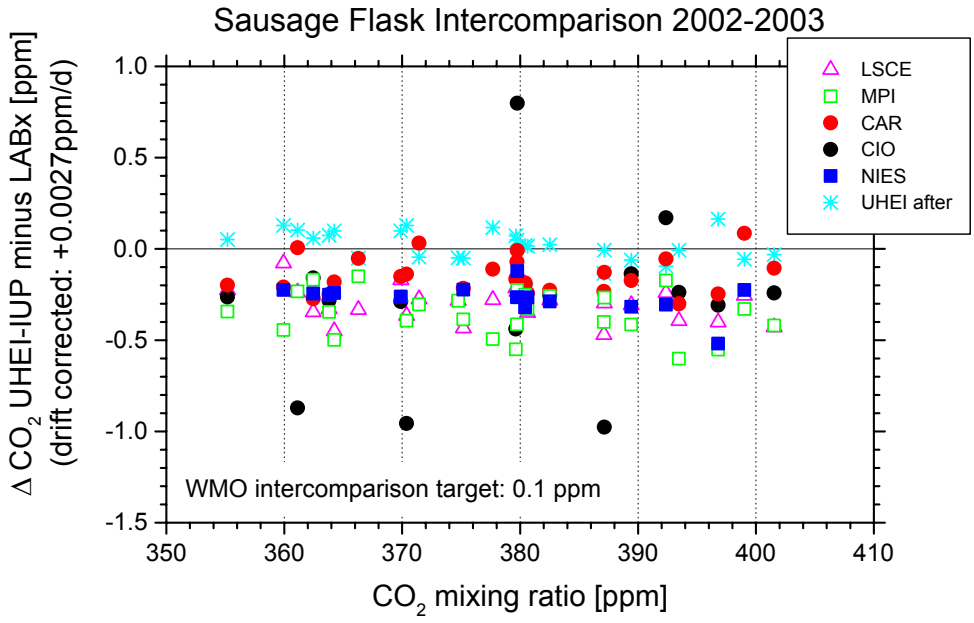

Figure 1a: Individual CO_2 mixing ratio differences between the flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") for the Sausage Flask Intercomparison 2002 and 2003 plotted against the mixing ratio of the filling tank determined at UHEI-IUP. Results have been drift corrected by +0.0027 ppm/day of storage.

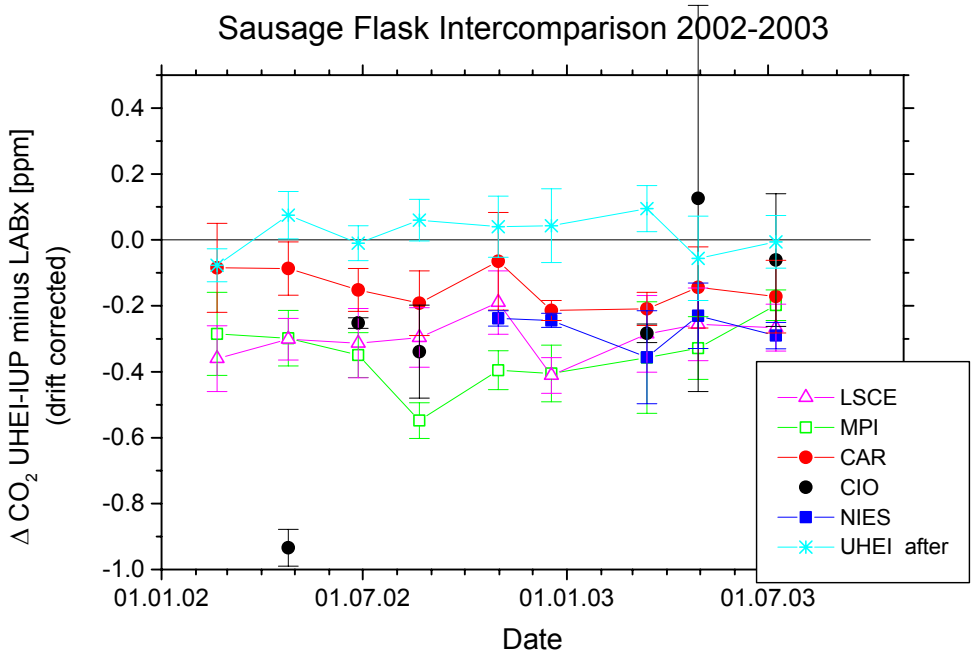

Figure 1b: Mean CO_2 mixing ratio differences between the three flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") of the nine different sausage batches plotted against time of filling at UHEI-IUP. Results have been drift corrected by +0.0027 ppm/day of storage.

$\delta^{13}C$-CO_2:

Figures 2a and 2b show the sausage flask results for $\delta^{13}C$-CO_2 evaluated and plotted in the same way as for CO_2 mixing ratios (i.e. Fig. 1a&b). As for the mixing ratios it is obvious that systematic differences are observed between the majority of labs. While UHEI-IUP and NIES results compare very well with only a very small variability over time, LSCE differences from UHEI-IUP show a considerable jump after sausage 5, when LSCE changed ceramics in the ion source of their mass spectrometer. This jump is also documented in the LSCE target gas, revised numbers will be reported by LSCE after re-calibration of the ms at the beginning of 2004. Most of the other laboratory differences are probably due to the fact that there still does not exist proper reference material for isotope measurements in atmospheric CO_2, and laboratories have to calibrate their mass spectrometers via either pure CO_2 reference gases or carbonate. This problem will hopefully be solved soon when MPI-BGC can provide reliable CO_2-in-air standards from carbonate reference material. The stability of the deviations is, however, in some labs still far from the target intercomparability of 0.01‰.

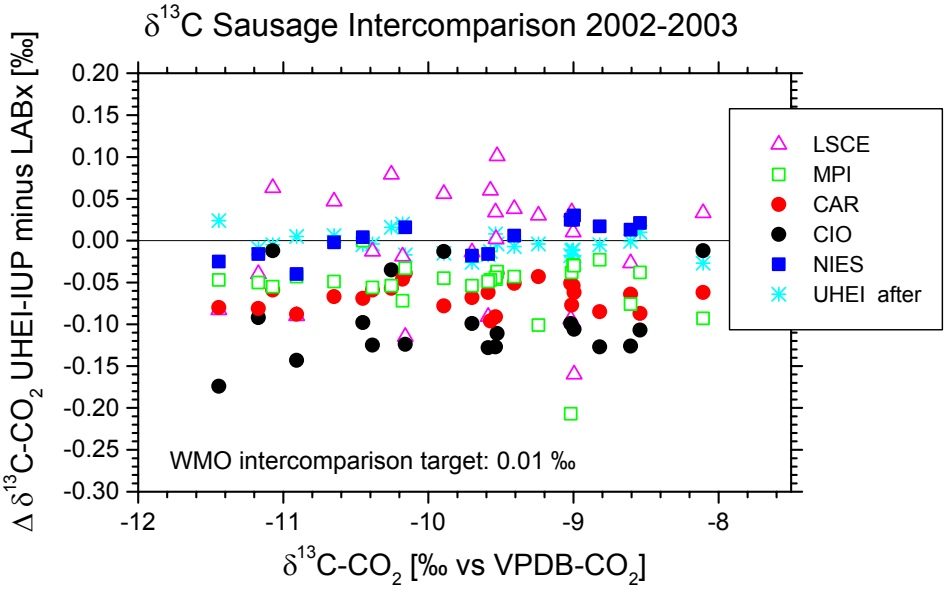

Figure 2a: Individual $\delta^{13}C$-CO_2 differences between the flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") for the Sausage Flask Intercomparison 2002 and 2003 plotted against the $\delta^{13}C$-CO_2 in the first flask pair determined at UHEI-IUP.

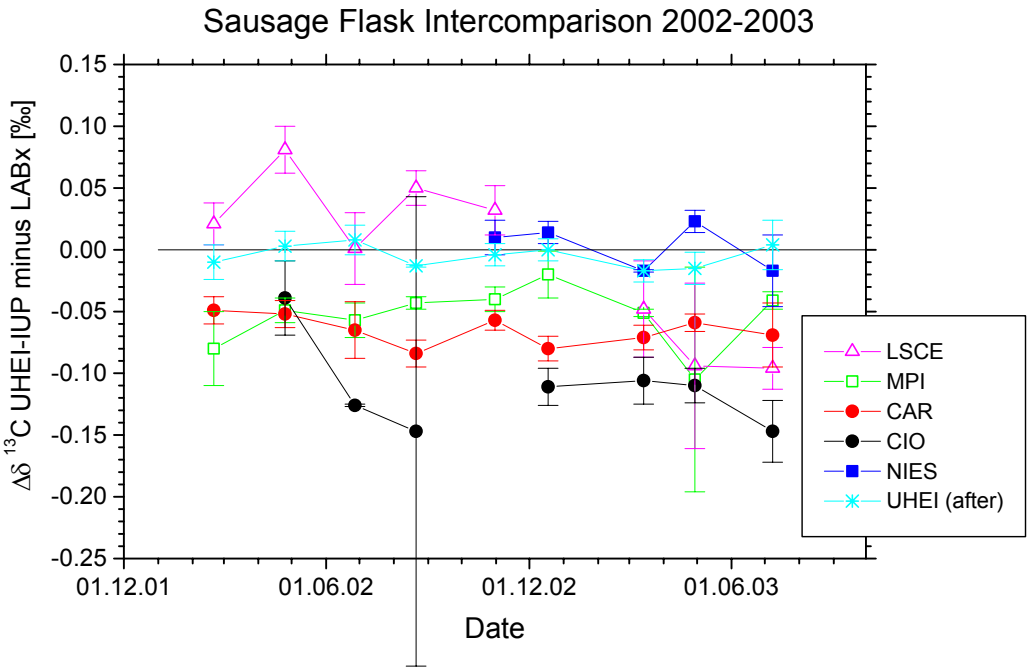

Figure 2b: Mean $\delta^{13}C\text{-}CO_{2\ differences}$ between the three flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") of the nine different sausage batches plotted against time of filling at UHEI-IUP.

$\delta^{18}O\text{-}CO_2$:

As in our earlier report in 2002, in the assessment of $\delta^{18}O\text{-}CO_2$ results from sausage flasks we excluded all values where pair differences in individual laboratories exceeded 0.1 ‰ or where only one flask gave a valid number. The pair difference turned out to be a very good indicator for ^{18}O isotope exchange, and thus contamination with traces of water at the glass surfaces during storage of the flasks. Although flasks had been repeatedly flushed and conditioned with dry sample air, there probably remained water traces on the flask walls from earlier fillings and respective isotope exchange effects are obviously still significantly disturbing the $\delta^{18}O\text{-}CO_2$ results. All valid data are plotted in Figures 3a and 3b. For $\delta^{18}O\text{-}CO_2$ there exist even larger scale differences between the individual labs than for $\delta^{13}C$, and also the temporal stability of the differences in absolute "permil" terms is much worse than for $\delta^{13}C\text{-}CO_2$. However, the intercomparability target for $\delta^{18}O\text{-}CO_2$ is more relaxed (0.05‰) than that for $\delta^{13}C\text{-}CO_2$ as the respective signals in the atmosphere are much larger. It will thus probably be met within the TACOS group after more experience was gained in proper flask conditioning.

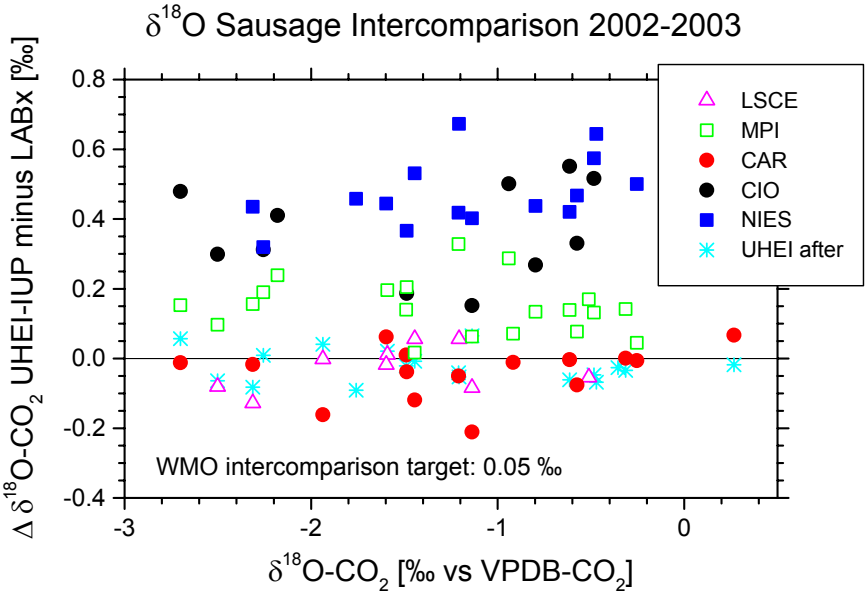

Figure 3a: Individual $\delta^{18}O\text{-}CO_2$ differences between the flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") for the Sausage Flask Intercomparison 2002 and 2003 plotted against the $\delta^{18}O\text{-}CO_2$ in the first flask pair determined at UHEI-IUP.

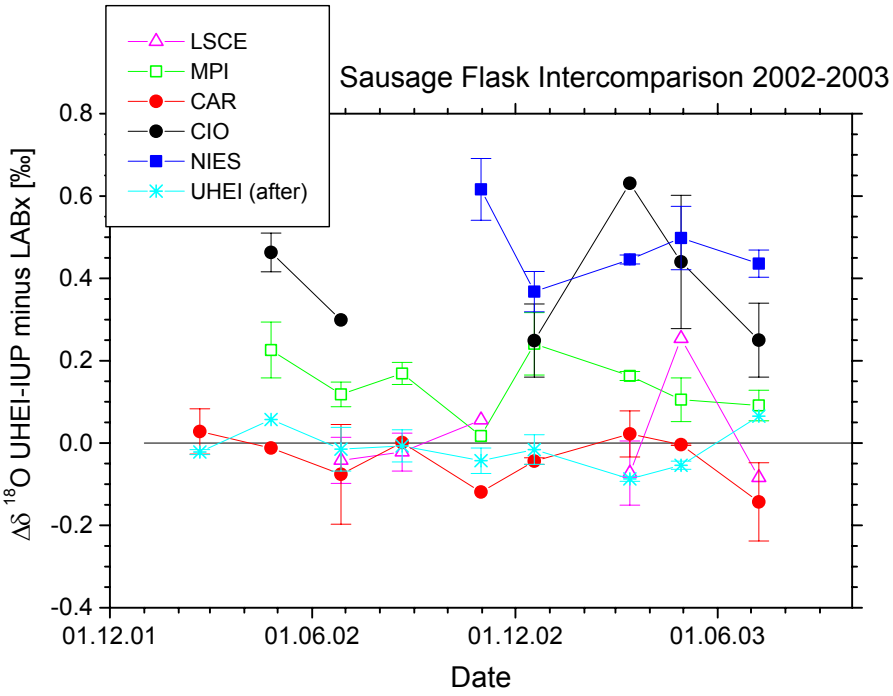

Figure 3b: Mean $\delta^{18}O\text{-}CO_{2\ differences}$ between the three flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") of the nine different sausage batches plotted against time of filling at UHEI-IUP.

CH_4 mixing ratio:

Figures 4a and 4c show the sausage flask results for CH_4 evaluated and plotted in the same way as for CO_2 mixing ratios. As the NIES laboratory is not on the same calibration scale (NOAA scale) as all other labs, an arbitrary value of 27 ppb was subtracted from the reported NIES CH_4 values. The scatter of individual flask pair deviations seems to be large, however, most deviations fall within the WMO interlaboratory comparison target of 2 ppb. Also the long-term stability of CH_4 differences in the majority of labs is on the order of 1.5 – 2 ppb. In Figure 4b deviations of all sausage pairs from that measured at CAR are plotted in order to find out if the precision of the Heidelberg CH_4 results is a limiting factor in comparability. Obviously, however, deviations from CAR show a similar scatter as those from UHEI-IUP.

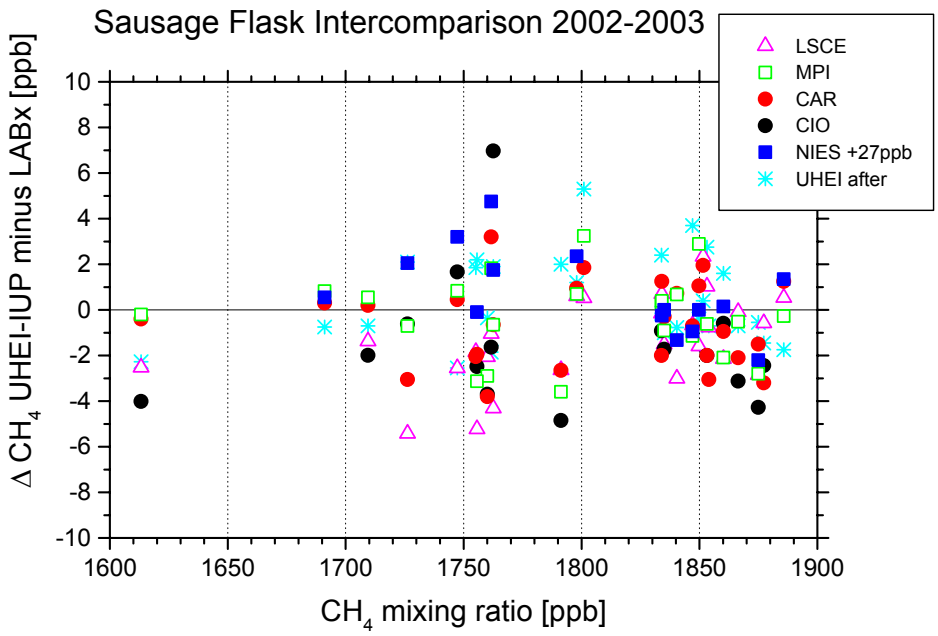

Figure 4a: Individual CH_4 mixing ratio differences between the flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") for the Sausage Flask Intercomparison 2002 and 2003 plotted against the mixing ratio of the filling tank determined at UHEI-IUP.

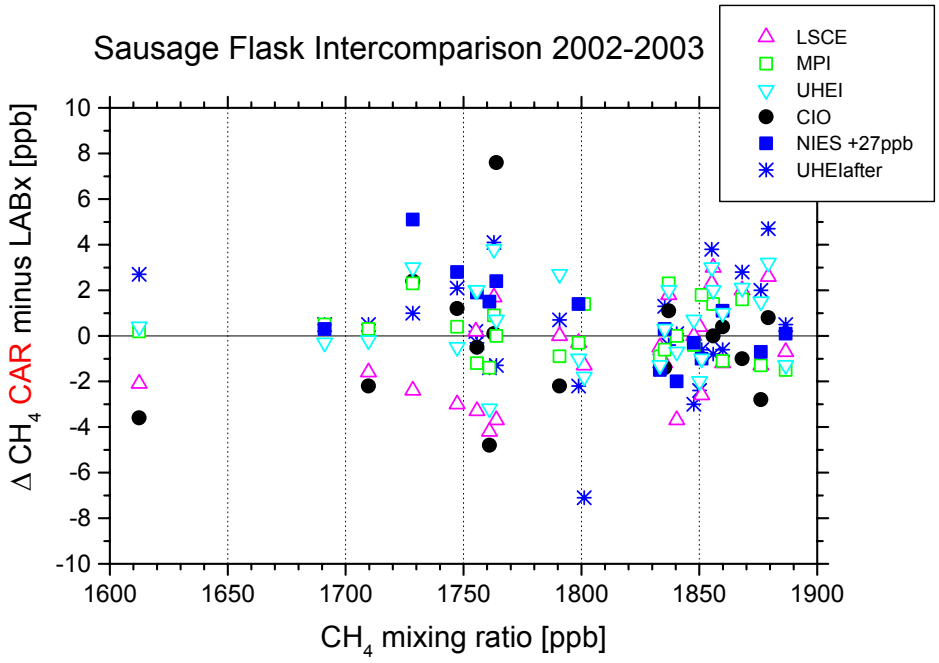

Figure 4b: Individual CH_4 mixing ratio differences between the flask pair means determined at CAR and individual labs ("CAR minus LABx") for the Sausage Flask Intercomparison 2002 and 2003 plotted against the mixing ratio of the filling tank determined at UHEI-IUP.

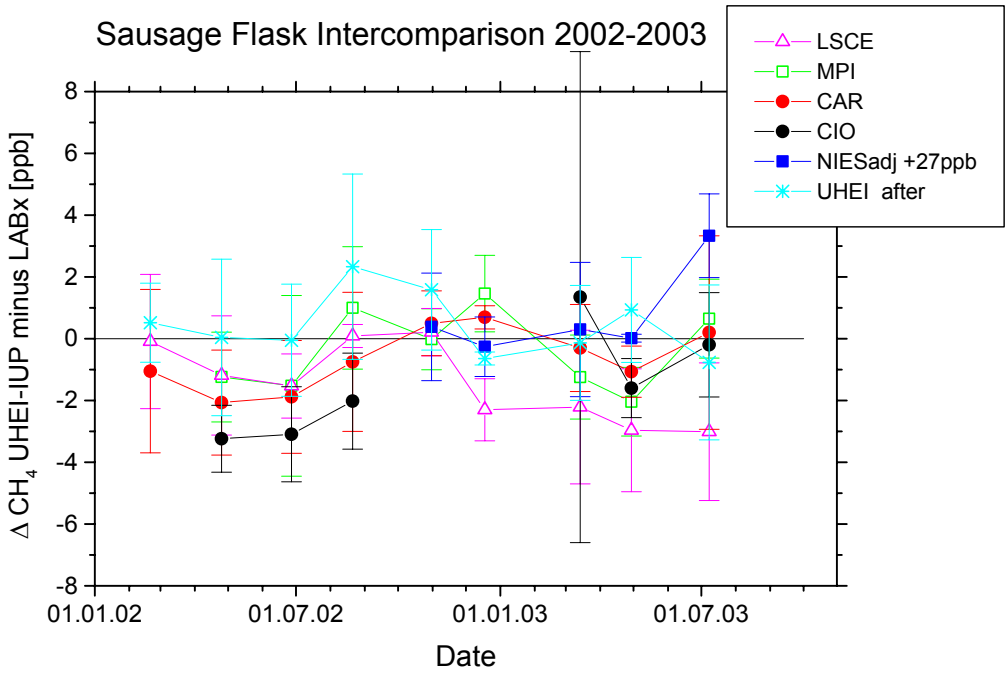

Figure 4c: Mean CH_4 mixing ratio differences between the three flask pair means determined at UHEI-IUP and individual labs ("UHEI-IUP minus LABx") of the nine different sausage batches plotted against time of filling at UHEI-IUP.

Summary

Table 1 summarises the mean laboratory differences for CO_2, $\delta^{13}C$-CO_2, $\delta^{18}O$-CO_2 and CH_4 for the nine intercomparison exercises performed during 2002-2003. Most labs show similar long-term stability in their flask differences, and mean values did not change significantly since 2002. This is a very promising result which brings the European Labs to the position to merge their data sets and compare them with networks outside of Europe. There is one step still missing, namely including the NOAA/INSTAAR laboratories in this exercise. First steps towards this direction have already been made but this will also exceed the current practical and logistics capabilities of UHEI-IUP. Within the new CarboEurope Project further extension has definitely to be made.

Table 1: Mean differences UHEI-IUP - LABx and standard deviation of all sausage pairs

	LSCE	CAR	MPI-BGC	CIO	NIES	UHEI after
ΔCO_2 Stdd CO_2	-0.298 ±0.097	-0.154 ±0.101	-0.353 ±0.122	-0.290 ±0.426	-0.272 ±0.083	0.018 ±0.086
$\Delta\delta^{13}C$-CO_2 Stdd $\delta^{13}C$	*-0.008* *±0.069**	-0.065 ±0.017	-0.053 ±0.037	-0.112 ±0.061	0.003 ±0.021	-0.004 ±0.014
$\Delta\delta^{18}O$-CO_2 Stdd $\delta^{18}O$	-0.027 ±0.064	-0.038 ±0.077	0.149 ±0.078	0.364 ±0.136	0.473 ±0.098	-0.023 ±0.046
ΔCH_4 Stdd CH_4	-1.560 ±1.899	-0.736 ±1.835	-0.369 ±1.311	-1.608 ±2.811	-26.245 ±1.828	0.425 ±1.953

* to be revised

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